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13. ABSTRACT (Maximum 200 words)
The objective of this 18-month feasibility study was to provide a portable energy production system that is simple to operate, has desirable energy density, and meets Army field requirements. Steps toward this goal were taken in three separate project tasks. Specifically, Task 1, Review and Regeneration, Task 2, Reactor Feasibility Demonstration, and Task 3, Integrated System Demonstration.
The review and regeneration study determined that it is not economically feasible to close the loop on the MAGNIC process by means of regenerating the $Mg(OH)_2$. The reactor feasibility demonstration determined that hydrogen can be produced from the MAGNIC reaction safely and controllably by controlling the temperature and reacting MAGNIC surface area. The reaction was found to proceed to completion in 2.5x stoichiometric water, and plugging and byproduct film inhibition were demonstrated not to be a problem. The integrated system demonstration showed that it is possible to recover heat from the reaction and utilized it to reduce the energy required to maintain a nominal rate of potable water production from a reverse osmosis desalination system. Based on the ratio of weight of product to weight of process hardware (mass efficiency), the MAGNIC powered system was found to be favorable when compared to diesel powered units.

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MAGNIC Hydrogen Production

Final Report

Prepared by:

P.C. Myers, Jr., John G. Cleland, and M. Wayne Turner

July 30, 1997

Presented to:

Dr. Richard Paur

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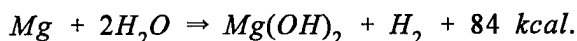
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Introduction

This study was initiated by the presentation in the U.S. by Russian scientists of the MAGNIC reaction process for producing clean hydrogen from the exothermic, water-splitting reaction



Salinity of the water (presence of Cl^- ions) promotes this reaction.

A proprietary alloy of magnesium, nickel and minor amounts of other elements had been developed at the St. Petersburg Technical Institute to improve this well-known reaction. The alloying mixture promotes the reactivity at the solid surface and the solid byproduct is segregated from the reacting alloy.

The Research Triangle Institute (RTI) first tested MAGNIC in the U.S. (Myers, et.al, 1996) and confirmed the hydrogen production rate and purity. The concept of MAGNIC hydrogen production and fuel cell operation was presented at US Army Offices in the Pentagon on February 16, 1995, where the need for improving Army desalination units was also first suggested. It was recommended that a proposal be submitted to the Army Research Office for evaluation of further investigations of MAGNIC feasibility as an Army energy source. This opportunity was advanced by the newly formed corporation MAGNIC International Inc. (MII) with technical support from RTI.

The investigations (proposed, implemented and reported herein) emphasized the following:

- Since MII wished to commercialize industrial-scale energy plants, small hydrogen power packs using MAGNIC would not be emphasized, but R&D would proceed at bench scale or pilot scale to demonstrate a process that could produce at least a few kW of power.
- A closed cycle for MAGNIC (including regeneration of magnesium from byproducts magnesium hydroxide or magnesium oxide) would be re-examined. A closed cycle would permit the only economically feasible commercial application of MAGNIC. Otherwise, magnesium fuel costs for hydrogen production were not competitive with other H_2 production methods such as methane reforming or water electrolysis. MII reports from Russian consultations supported recycle feasibility.
- The primary goal for an Army application would be a high-energy-density (kWh/kg) hydrogen source for operating a fuel cell. This goal led to two complimentary objectives:
 - 1) Apply a MAGNIC hydrogen source and fuel cell to power a desalination unit for troops in the field, since the Army was considering lighter, simpler desalination systems with low detectability. Also, salt water is a reactant in

desalination systems with low detectability. Also, salt water is a reactant in the MAGNIC process and its use in a desalination unit would not impose an additional mass penalty on the MAGNIC generator. A reverse osmosis desalination (ROD) process was chosen to duplicate Army preferences and because of its high efficiency at small scale.

2) Utilize the heat of reaction of the MAGNIC process to improve process efficiency or otherwise reduce system mass. The heat recovery technique developed was one of improving ROD membrane efficiency for water filtration by increasing water temperature. This reduces the required pressure for the ROD membrane and lowers pump power.

- Other advantages of MAGNIC would be demonstrated, such as stable storage, safe and simple handling, and low heat/visual/audible signatures in the field.
- A prototype system for Army application, transportable on a light vehicle, would be developed and demonstrated. The system would be safe and simple to operate.

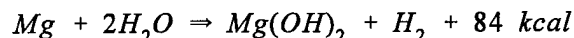
The objectives above were completed, resulting in varying degrees of success as discussed in the following report. A figure of merit (defined as mass of potable water produced per mass of desalination system required) was applied for comparative evaluation.

The MAGNIC hydrogen generator, fuel cell, and reverse osmosis unit can provide a desalination system that competes with or improves upon small (<100 gallons per hour) diesel-engine-powered desalination units. MAGNIC fuel is more costly but potentially easier to handle than diesel fuel. However, the MAGNIC byproduct is a paste of $Mg(OH)_2$, which hinders easy removal. MAGNIC generators and fuel cells are quieter, cleaner, and cooler than diesel engines. MAGNIC operation would require more labor, but does offer reduced mass and cost advantages. However, MAGNIC advantages do not appear to offer a quantum leap improvement that would justify replacing a reliable, compatible Army approach to desalination.

Nor is there support for a closed cycle of the magnesium reactions or potential for extensive commercialization of hydrogen generation by MAGNIC. RTI and MII have evaluated the realistic potential of MAGNIC, and consider the results a success in terms of providing the necessary factual data for conclusions.

1. Statement of Problem Studied

MAGNIC is a material and a reaction process for producing hydrogen gas and heat by a thermochemical, water-splitting reaction. The MAGNIC material is a magnesium/nickel alloy, developed in Russia (Kirrilov and Serebrennikov, 1994, 1995). As part of this project, MAGNIC has also been produced in the U.S. using the Russian formula. The MAGNIC process can generally be defined by the reaction:



The magnesium/nickel alloy reacts with water in the presence of catalytic electrolytes to produce hydrogen, heat, and a magnesium hydroxide byproduct. The hydrogen from the reaction can be converted to electricity in a proton exchange membrane (PEM) fuel cell, the heat can be captured to drive a process (e.g., evaporation) or used to heat a medium (e.g., reverse osmosis feed water). The magnesium hydroxide can be used as a waste treatment alkali for acid neutralization.

The primary objectives of this study were to: (1) investigate the possibility of regenerating the primary reaction byproduct, magnesium hydroxide, to magnesium; (2) demonstrate the MAGNIC reaction to be safe and controllable, and show that large amounts of excess water are not required; and (3) demonstrate the feasibility of a portable energy production system used in conjunction with a reverse osmosis desalination unit.

The schedule for the study, broken down into project objectives, is shown in Figure 1. The Review and Regeneration Study was proposed to be performed in two phases. The initial phase, extending from July 1, 1995 to October 1, 1995, included intensive review of literature on the process and an evaluation of the feasibility of regenerating the magnesium hydroxide byproduct back to magnesium. For this objective, the second phase set aside from January 1, 1996 to July 1, 1996 was intended to include laboratory experimentation on feasible regeneration options. This phase of the Review and Regeneration Study was not pursued. The Reactor Feasibility Study was performed during the period from July 1, 1995, to May 1, 1996. The Integrated System Demonstration was performed from January 1, 1996 to May 1, 1997.

The objective of investigating regeneration of the primary reaction byproduct, magnesium hydroxide, to magnesium was met by the performance of an extensive literature review and consultations with experts in the U.S. and Russia. This task was performed in an effort to identify the technical and economic feasibility of closing the loop on the hydrogen production from magnesium process. If an economical solution to regenerating the hydroxide byproduct back to magnesium existed, then MAGNIC hydrogen production would be a viable alternative to fossil fuels and conventional batteries for numerous applications. The review and regeneration study performed by MAGNIC International Inc. and Research Triangle Institute involved a search of Russian literature, a search of the extensive database at Research Triangle

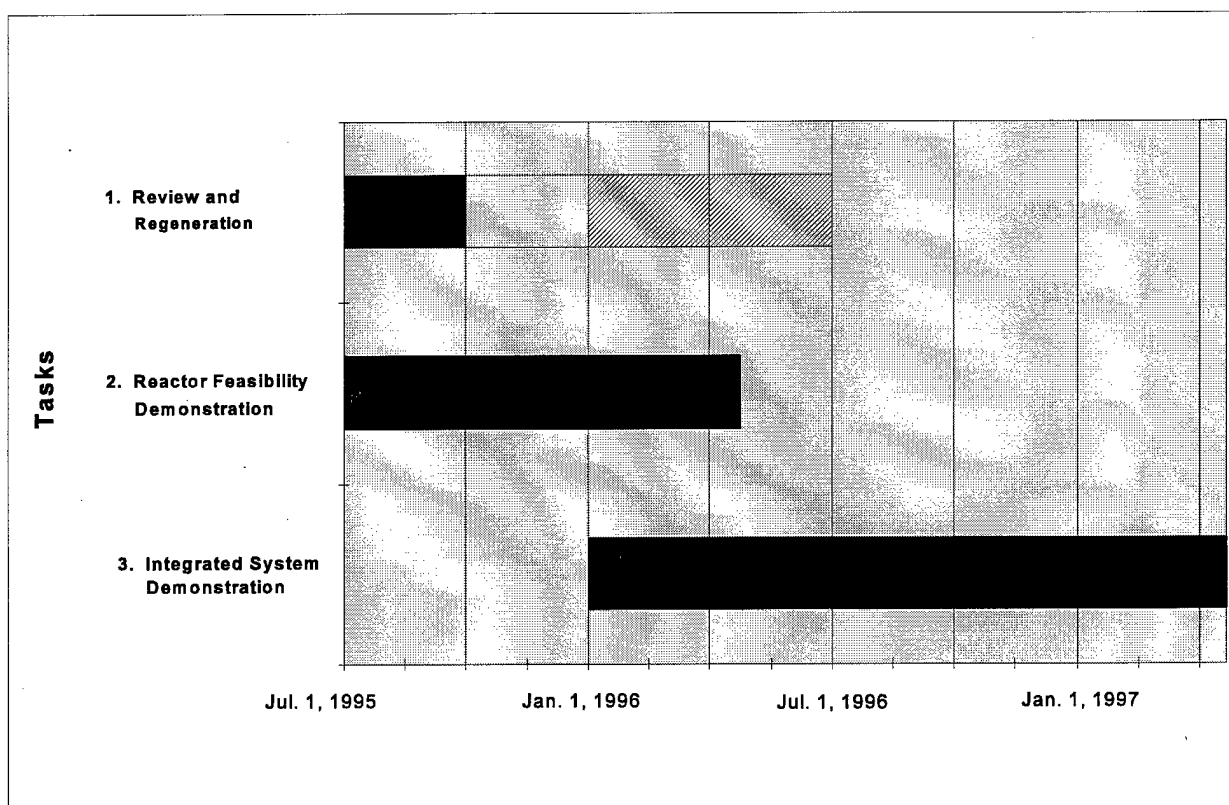


Figure 1: Project Schedule

Institute's library, a search of resources available at NCSU and Duke University libraries, a search for manufacturers of magnesium in the United States by means of the Thomas Register, and consultation with a number of experts in the field of metal oxide regeneration.

Reactor feasibility was established by a series of experiments performed in two bench-scale reactors. Initial experiments were carried out in a micro-scale, 1 liter glass reactor. The micro-scale experiments were performed to verify empirical data provided by the Russian consultants. An additional objective was to provide answers to questions from the Army Research Office relating to: (1) the amount of water required to drive the reaction to completion, and (2) whether or not the oxide film generated during the reaction would inhibit the reaction from proceeding to completion. Later bench-scale experimentation was performed in a 1 ft³ stainless-steel reactor operated nominally at 158°C and 6 atm. This reaction system offered varying filter medium, water recycle to the reactor from a knockout pot in the product stream, a back pressure regulator to allow variable operating pressures in the reactor, and automatic acquisition of reaction temperatures, pressure, and flow rate. Experiments in this unit provided insight into the effects of operating temperature, operating pressure, fuel geometry, and water requirements on the overall process.

The final objective of demonstrating the feasibility of a portable energy production system used in conjunction with a reverse osmosis desalination system was met by the construction and operation of a reaction system in the lab that integrates the reaction of 2 kg of MAGNIC with a reverse osmosis water desalination unit to produce 25 gallons per hour (gph) of potable water. Use of MAGNIC-produced power for desalination was chosen due to the possibility of waste heat utilization for increased potable water production. Other advantages relate to the visual, audible, and heat signature associated with the diesel engines presently being used in Army field desalination units. The fact that the salt water being used in the desalination process can be used as a reactant in the MAGNIC reaction eliminates much of the overall system mass required to be transported into the field.

The power produced from the reaction of 2 kg of MAGNIC in a salt water solution, assuming the use of a fuel cell with 50% efficiency, is 3.04 kWh. The integrated desalination unit consists of a stainless-steel jacketed reactor, a plate heat exchanger, a Sea Recovery® reverse osmosis water desalination system, a bubble condenser, a fuel cell simulator, and a complete data acquisition system. The unit is mounted on a mobile skid which is 2.5 ft. wide x 5 ft. long x 4 ft. tall. The overall process mass efficiency, defined as pounds of water produced per hour per pound of system weight, is 0.65. The experiments were performed with approximately 4x stoichiometric water, at atmospheric pressure, and with varying fuel geometries to achieve a stable hydrogen production rate with rapid startup and shutdown to maximize steady state operation.

2. Summary of Results

The results of the investigation into the use of the MAGNIC reaction for mobile power production and desalination are summarized below. The following sections expand on these conclusions.

With respect to the general MAGNIC reaction, the following conclusions have been reached:

- Regeneration of magnesium hydroxide byproduct back to magnesium is not economically feasible. (See Section 2.1 *Review and Regeneration Study*)
- A reaction can proceed to completion in as little as 2.5x stoichiometric water. (3.75 times the amount of MAGNIC fuel)
- In 2.5x stoichiometric water, the byproduct does not prevent water from reaching the exposed surface of the MAGNIC fuel.

With respect to the application of MAGNIC for power to operate a desalination unit, the following conclusions have been reached:

- The use of MAGNIC-generated power for reverse osmosis desalination in field applications has distinct mass and cost advantages over diesel generated power. This is true regardless of the use of heat recovery. (See Sections 2.5 *Field Operation Characteristics* and 2.6 *Costs*)
- When heat recovery is employed to warm reverse osmosis feed water, the system mass can be reduced due to decreased steady-state power consumption. The ratio of pounds of potable water produced to total system weight is 35% better for MAGNIC using heat recovery than for diesel-based units of equivalent production capacity. (See Section 2.5 *Field Operation Characteristics*)
- Retrieval of heat from the bubbling of product gas and steam through the reverse osmosis desalination feed water is not a significant contributor to the heat recovery process. The amount of heat recovered does not justify the added mass of the device. (See Section 2.2 *Design and Construction of Integrated Demonstration Unit*)

2.1 Review and Regeneration Study

The review and regeneration study was performed at Research Triangle Institute by Dr. William Gutknecht of RTI and Marina Semenova of MAGNIC International, Inc. (Myers, et. al, 1996). The study included extensive searches of resources at Research Triangle Institute's library, NCSU and Duke's libraries, Thomas Register's list of United States magnesium producers, and the databases of Teltech, Inc., a professional information retrieval firm, accessing over 1700 databases, a worldwide network of technical experts, and a comprehensive equipment vendor information database. Additionally, several experts in the field were consulted on the feasibility of regenerating magnesium hydroxide to magnesium. The list of consultants includes Dr. Rustam Mirsoev (St. Petersburg State Technical University, St. Petersburg, Russia), Frank Lynch (President, Hydrogen Technologies, Inc., Denver, CO), Dr. Jim Hillis (Dow Chemical, Freeport, TX), and Bryon Clow (International Magnesium Association, McClean, VA).

The result of the study is that no new breakthroughs have been made in the regeneration process that would make the regeneration of magnesium hydroxide to magnesium an economically feasible option. The methods of magnesium production include electrolysis, carbothermic reduction, silicothermic reduction, and plasma-powered processing. Recent advancements in these methods have been process efficiency improvements which are not significant enough to overcome the expenses required for the handling, transportation, and processing of the magnesium hydroxide produced in the MAGNIC reaction.

2.2 Reactor Feasibility Demonstration

The primary objective of the reactor feasibility demonstration was to show that a MAGNIC-driven reaction system can safely be operated for controllable hydrogen production. To do this, a semi-batch reaction system with extensive data acquisition and a detailed control scheme was

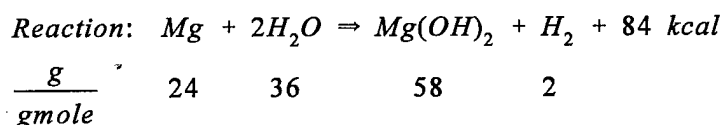
constructed. The reactor also addressed several concerns raised by the Army. The concerns were that: (1) the minimum amount of water required to drive the reaction was too large; (2) the reaction on the MAGNIC surface would stop because of film buildup of reaction byproduct; and (3) byproducts would become entrained in the product gas and plug piping throughout the system. A final consideration in the design of the batch reactor was that it have the ability to scale up and be used for the integrated feasibility test.

2.2.1 Micro-Scale Glassware Experiments

Prior to testing with the 1 ft³ (~28 l) semi-batch reactor, several experiments were performed using the 1 liter glass reactor. These tests were performed to address questions 1-3 posed by the Army Research Office. Results of these tests helped to determine the minimum water requirement and the effect of the magnesium hydroxide byproduct on the reaction kinetics.

Minimum Water Test

According to the stoichiometry of the magnesium-water reaction, only 1.5 ml H₂O is needed per gram of Mg:



However, the magnesium hydroxide byproduct is hydrophilic, and can form weak, intermolecular hydrogen bonds with up to three H₂O molecules. Over time, MAGNIC will react with this water and dry the byproduct, but this reaction can be slow. This indicates that excess water is needed for the reaction to go to completion. A test was performed to determine how much water is actually needed for the reaction to go to completion in a reasonable amount of time. The data from this experiment is shown in Table 1.

Experimental results showed that the MAGNIC reaction can start quickly and proceed to completion in as little as 2.5x stoichiometric water. The reaction will go to completion in as little as 2x stoichiometric water, but requires more extended amounts of time. The byproducts of the MAGNIC reaction have different properties in varying amounts of water.

When less water is used, the reaction takes place with the water adsorbed in the byproducts. The final byproduct is a very thick light gray material. When excess water is used in the reaction, the byproducts are darker gray, and watery. As long as the MAGNIC remained submerged and more than 2.5 x stoichiometric water was present, the reaction times were consistent.

Table 1. Minimum Water Test Results

Test ID	Weight MAGNIC (g)		Ratio Water: MAGNIC	Weight Byproduct (g)		Time (min)
	Initial	Remaining		Wet	Dry	
1	10	4.4	2	30.0	15.1	37
2	20	5	2	67.2	42.0	60
3	30	7	2	101	70.1	75
4	20	0	2.5	78.4	58.8	24 hr*
5	9	0	2.5	41.1	25.3	90
6	8.98	0	2.5	33.3	17.2	120
7	20	0	4	---	---	50
8	20	0	4	133.1	---	65

*Elapsed time between measurements.

Reaction Rate Determination

For test purposes, Dow Chemical Inc., of Colorado was able to produce the magnesium alloy following the procedure provided by Russian consultants. Rate-determining tests were performed to identify differences between the Dow MAGNIC and the imported Russian MAGNIC. These tests were performed in boiling conditions at atmospheric pressure, which allowed for easily reproducible experiments. Data for this experiment is shown in Table 2.

Table 2. Reactivity of MAGNIC

Origin	Test ID	Sample Weight (g)	Reaction Time (min)	Gas Produced (cfm)
Dow	1	7.5	180	0.157
Dow	2	15	165	0.492
Russian	1	7.5	175	0.148
Russian	2	15	165	0.478

The tests showed that the amount of time required for the Dow MAGNIC to react is very similar to that of Russian MAGNIC. This indicated that the MAGNIC produced by Dow should conform to the empirical data and reaction kinetic calculations provided by the Russian scientists.

Determination of Optimal Plate Thickness

Empirical calculations performed at 100°C and 1 atm show that a single flat side of MAGNIC should react 3.5 mm in approximately one hour. This means that plates which are approximately 7 mm thick with the reaction occurring on both faces should react in one hour. The data for the experiment verifying these calculations is shown in Table 3. As seen, the

average experiment with 7 mm thick squares of MAGNIC took 74 min. Tests with 6 mm thick squares required an average of 67 minutes. Thus, for the desired one hour reaction time, squares that are slightly less than 6 mm thick are ideal.

Table 3. Thickness vs. Reaction Time

Test ID	Sample Thickness (cm)	Sample Weight (g)	Reaction Time (sec)
1	0.6	15.8	66
2	0.6	15.7	68
3	0.7	17.7	74
4	0.7	17.8	74

2.2.2 Bench-Scale Reactor

The final reactor feasibility demonstration was performed with the 1 ft³ bench-scale reactor to confirm controllable hydrogen production using a product gas condenser which recycled the water from the product gas stream back to the reactor. The design and operation of the reactor addressed all of the issues raised by the Army relating to water required to drive the reaction to completion, film inhibition, plugging of the system due to frothing, and adequate control of the system. The reactor was designed to operate over a one hour period, producing enough pure hydrogen for 5 kWh electrical power in a fuel cell operating at 50% efficiency. The reactor also incorporated a cassette design in which the unreacted MAGNIC was loaded and the magnesium hydroxide byproduct was contained and removed. One continuous reaction scheme that was considered from this design included two such reactors operating alternately to provide continuous hydrogen production during the integrated field demonstration.

Reactor Design

The reactor has a volume of 1 cubic foot and is designed to operate at pressures to 10 atm and temperatures to 200°C. It is constructed out of ten gauge 316 stainless steel with a flanged lid. The reactor weighs 86 lbs. including the 24 lb. lid. It has several ports on the top, bottom and side, which are used for various process connections and instrumentation. These include the gas exit, liquid level gauge, pressure relief valve, reactor drain, recycle water feed, and various pressure gauge and thermocouple ports. The MAGNIC cassette which slides inside the reactor is constructed from 316L stainless, as are the 1/4" rods from which the MAGNIC is suspended. The cassette mounts inside the reactor on two permanent screws. Cassette distance from the bottom of the reactor can be adjusted prior to the experiment. Martin Petersen Inc. of Waukesha, WI fabricated the reactor and the cassette for RTI. A filter (used to control frothing) consists of two stainless-steel rings with stainless-steel mesh welded onto them. A 1/2" thick layer of fine stainless-steel wool is held between the rings. The filter was designed and fabricated at RTI.

Reaction System Design

The reaction system centers around the batch reactor and condenser. The P&ID for the reaction system is shown in Figure 2. The condenser is a Mueller Accu-Therm plate and frame heat exchanger. The hydrogen and condensed steam feed into a knockout pot from the condenser. The knockout pot has an on-off liquid level detector which lets the operator know if there is water in the pot at or above 2". Pressure drop through the heat exchanger and water recycle is minimal, which allows for a gravity fed recycle stream. Hydrogen gas exits the top of the knockout pot and passes through a desiccant trap prior to reaching the back pressure regulator (BPR). The BPR is a passive spring-loaded flow restriction device, which can be used with a pressure gauge to maintain system pressure. After passing through the BPR, the hydrogen travels through a dry test meter which records the amount of gas produced. Water is initially fed into the reactor (gravity feed) from a 25 L tank located 3-1/2 feet above the reactor. The ball valve located at the bottom of the reactor is used to remove water from the reactor in the event of an emergency, and to remove water and byproducts after runs. The system is designed to operate at pressures of up to 10 atm (147 psig.) The individual maximum pressures for the main components of the system are at least 10 atm.

Control Scheme

There are many controllable process variables which influence the reaction. However, the two which have the largest influence on the reaction are the surface area of MAGNIC and temperature.

The reactor temperature is the single most important factor controlling the MAGNIC reaction rate. Extensive studies have been performed in Russia examining the effect of temperature on reaction rate, mostly at temperatures less than 100°C (Myers, et.al, 1996). The results show that the reaction rate increases exponentially as the temperature is increased. Since water begins to boil, the reaction reaches a maximum of 100° C at atmospheric conditions. To further increase the temperature in the reactor, the pressure must be increased. The relationship between pressure and temperature in the boiling system makes pressure control critical to the success of the reactor. The back pressure regulator at the outlet of the reaction system can be used to alter the pressure, and therefore the temperature of the boiling solution. The maximum operating pressure for the reactor is 6 atm (88.2 psig), which corresponds to 158.8°C.

The MAGNIC reaction occurs when the surface of the alloy contacts water and catalytic ions (i.e., Cl⁻). The reaction rate of a given mass of MAGNIC is dependent on the amount of surface contacting the salt water solution. This indicates that an effective control method is to determine a MAGNIC geometry that will have constant surface area submerged in the water.

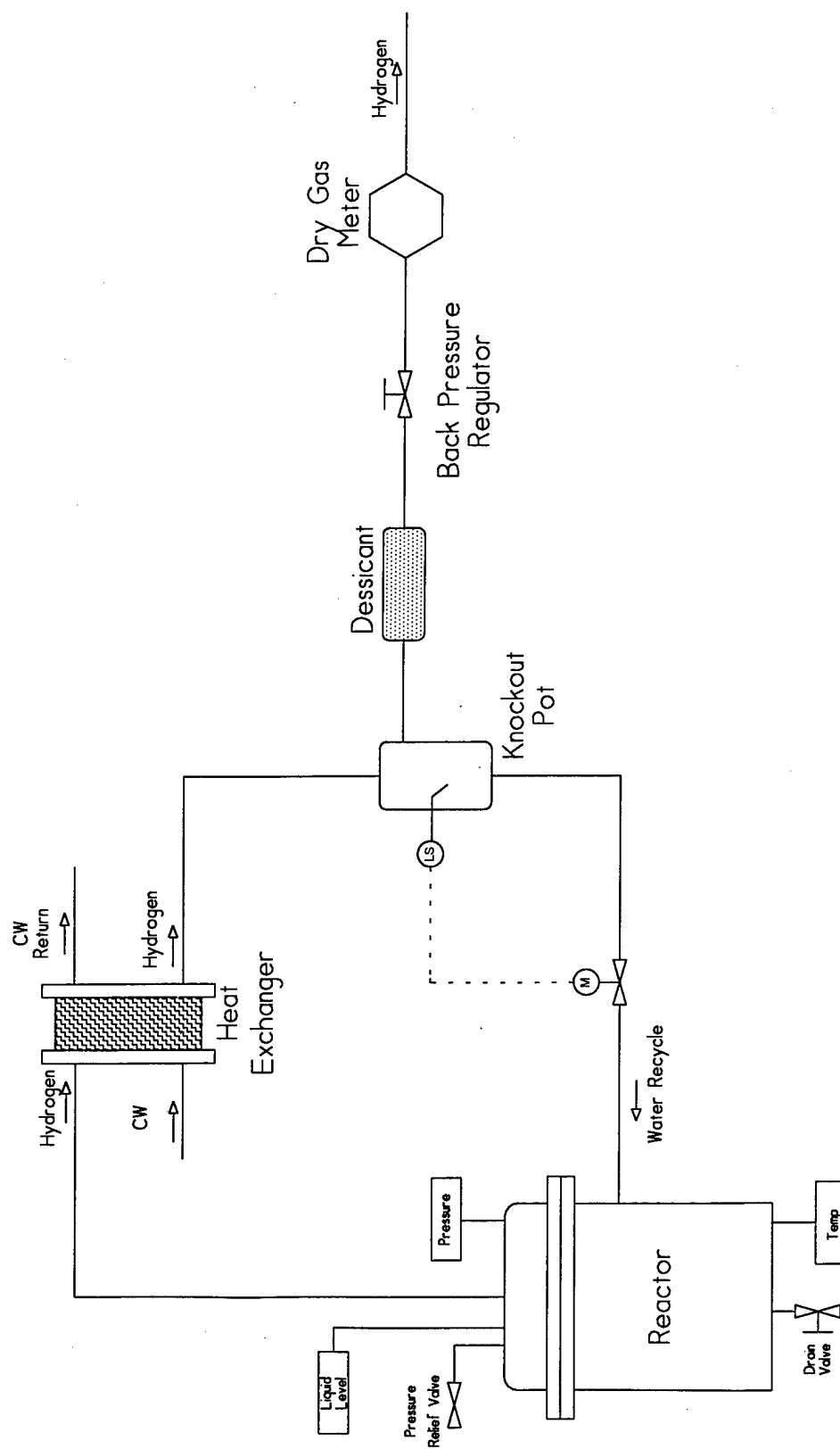


Figure 2. Bench-Scale MAGNIC Reaction System Design

To maintain a continuous reaction rate and stable hydrogen production, plates that have constant surface areas on their sides were used. Enough water was recycled to assure that they remained submerged. To reduce the reaction rate, the water recycle could be slowed down, which deprives the top of the plates of water and reduces the reacting surface area.

Reactor Feasibility Demonstration Results

Numerous experiments were performed in the bench-scale reactor. The hydrogen production rate was found to be controllable by controlling the level of 3.5% NaCl solution in the reactor, the pressure of the system, and the geometry of the MAGNIC loaded into the system. Figures 3, 4, and 5 show respectively the hydrogen flow rate, pressure, and temperatures associated with a typical experiment in the bench-scale unit. Spikes in the hydrogen flow rate are a result of the water recycle. Water that exited the reactor in the form of steam was condensed in a plate type heat exchanger and collected in a condensate knockout pot. When the water level in the knockout pot activated the level switch, a valve was opened. Condensate drained from the knockout pot back to the reactor, thus recycling the water. The addition of the recycled water cooled the reactor, reducing the amount of steam produced by the boiling system, and momentarily dropping the pressure in the reactor. The BPR would act at this point to reduce the flow out of the system until the pressure built again to the preset pressure on the BPR. It was hypothesized that the effects of no hydrogen flow during the recycle operation could be eliminated by implementing a continuous recycle, eliminating the recycle completely, or adding a capacitance volume and another regulator following the BPR that would hold a predetermined amount of hydrogen which would flow to the fuel cell during the periods of recycle. It was concluded that the water recycle provided no real benefit to the reaction as it related to the integrated system approach. Since the integrated system includes water desalination, salt water would be available and conservation of water through a recycle process would not be necessary.

Several fuel geometries and orientations were used in order to increase the amount of time at steady state operation relative to overall experiment time. Due to their high surface area, MAGNIC dust and flakes (collected from milling of ingots) were used to heat the system and reduce time to start. The flakes were loaded into cloth sacks and placed under the fuel cassette. The sacks allowed water to pass through to react with the flakes. The sacks also contained the magnesium hydroxide byproduct for easy removal once the experiment was complete. It was found that 150 grams of MAGNIC flakes heat up the reactor to 60 °C in as little as five minutes.

The reaction was initiated by the addition of the 3.5% NaCl solution to the reactor. The reaction was allowed to proceed to completion uninterrupted during most experiments. Twice, the reaction was stopped by removing the water from the MAGNIC to show that the reaction could be stopped in the event of an emergency. Water-fuel separation was achieved by opening a 2" ball valve at the bottom of the reactor, removing the water from the fuel cassette, and stopping the reaction.

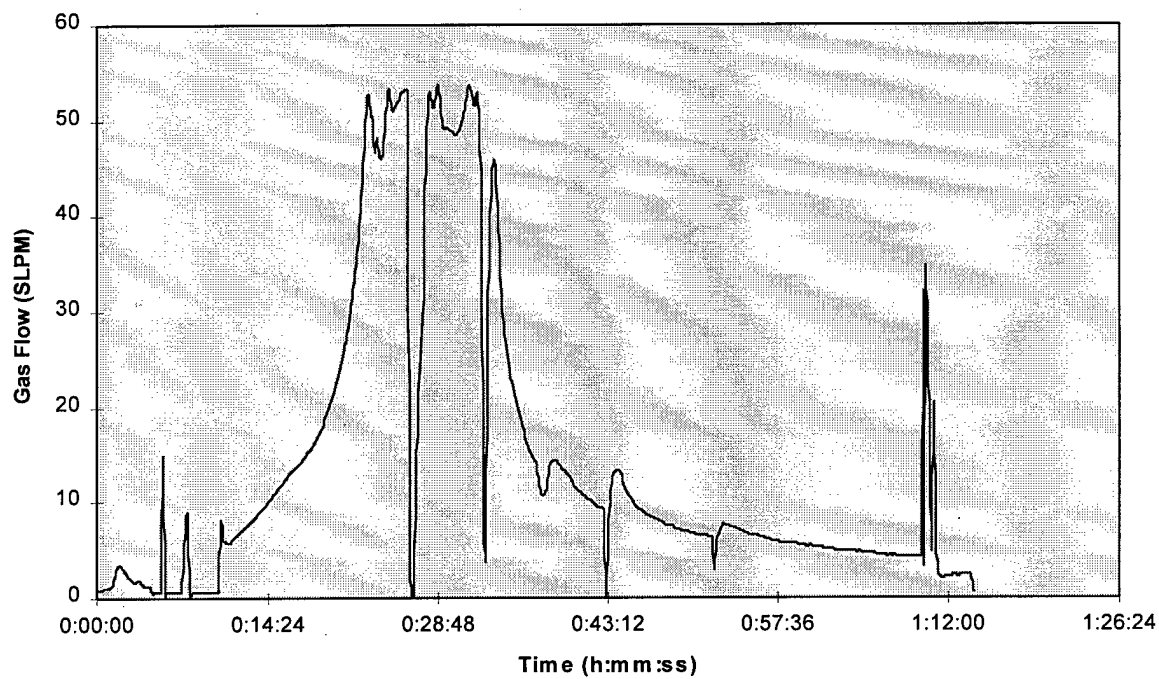


Figure 3. Hydrogen Flow Rate: Bench-Scale Experiment.

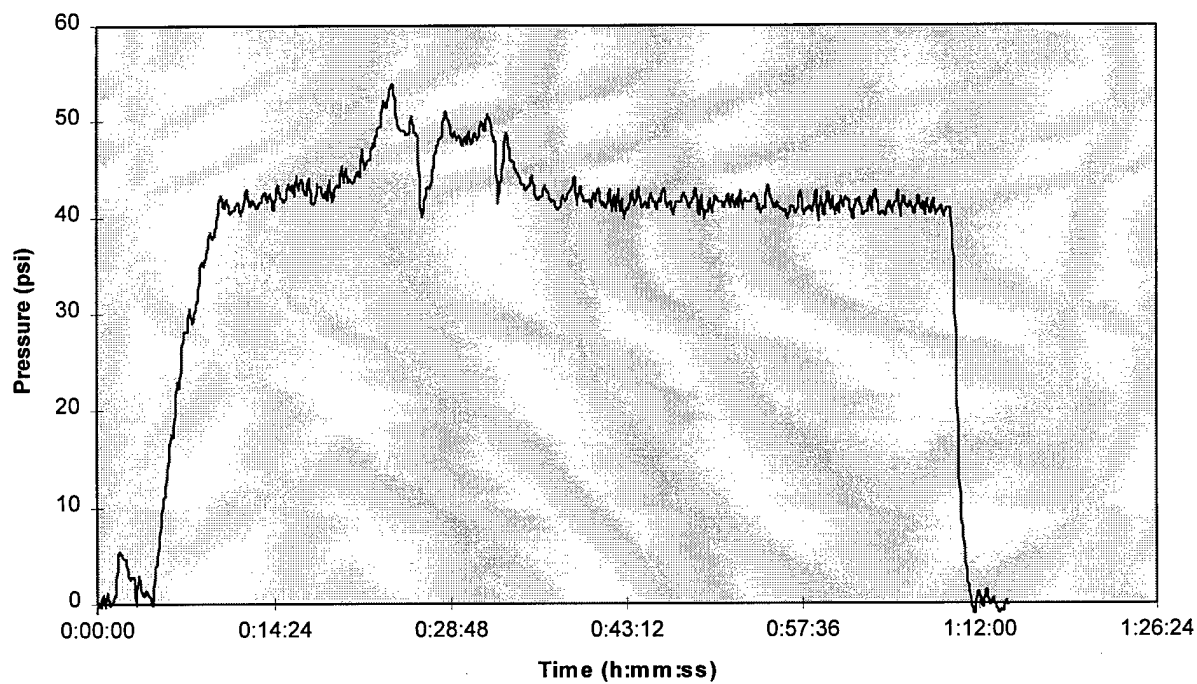


Figure 4. Reactor Pressure: Bench-Scale Experiment.

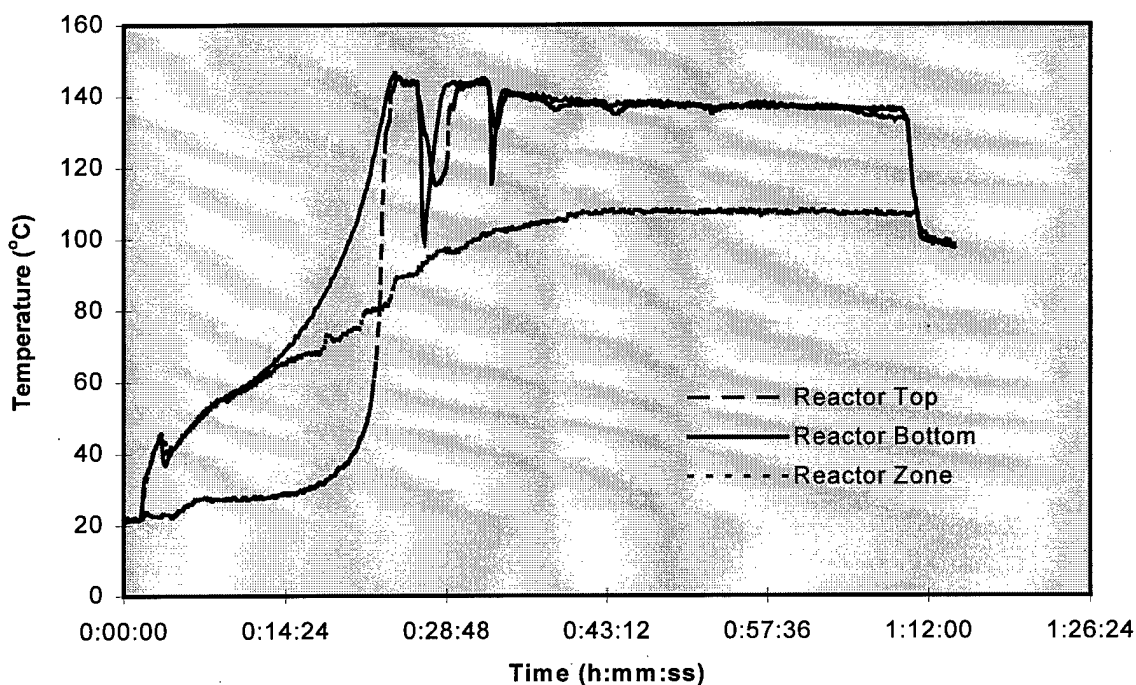


Figure 5. Reactor Temperatures: Bench-Scale Experiment

It would have been possible to control the rate of reaction based on the level of the 3.5% NaCl solution in the reactor. Changing the liquid level would change the amount of MAGNIC in contact with the 3.5% NaCl solution thus changing the rate of hydrogen production. The system pressure was also used to control the rate of hydrogen production. However, this was a predetermined value set by the back pressure regulator. The higher the system pressure the higher the boiling point of the 3.5% NaCl solution. The higher boiling temperature allowed for a higher overall rate of hydrogen production.

2.3 Design and Construction of Integrated Demonstration Unit

An important consideration for the MAGNIC hydrogen generator design was selection of nominal operating temperature and pressure. Operating at or above saturation temperature results in steam vaporization of process water. This water can be condensed and returned to the generator but requires more complex design. Operating at saturation or super heat steam conditions produces gas and steam pressure from which work could be recovered for ROD pumping. However, the reaction generator vessel strength must be increased for higher pressure, introducing additional mass penalty. The reaction also proceeds more rapidly at increased temperature. The MAGNIC fuel load must be retailored to fuel cell and pump demand. Operation is naturally less stable at high temperatures. Hydrogen temperatures can not exceed the limits for a fuel cell and the saltwater brine temperature can only reach certain limits

(well below steam saturation temperatures) imposed by the ROD membrane. High pressure operation is better accomplished in a continuous generator, either with plug flow or mixed flow, rather than a batch reactor. A continuous reactor will substantially decrease generator volume but increases complexity and control requirements. For reasons of simplicity and safety, it was decided to proceed with a generator operating near ambient pressure.

The integrated system operating at ambient pressure was built to provide safe, flexible experiments that allow varied experimentation utilizing automated data acquisition. A schematic representation of this system is shown in Figure 6. The major parts of the system are the brine heat exchanger, the reaction vessel, the fuel cell heat recovery simulation unit, the bubble condenser, the reverse osmosis desalination system pumps, and the reverse osmosis desalination system membranes. The following sections cover each of these components as the reaction vessel, the reverse osmosis desalination system, and the heat recovery system.

The Reaction Vessel

The reactor is a 1m long, 8" diameter cylinder which is mounted horizontally on the unit. The vessel is surrounded for its entire length by a jacket composed of a ten inch diameter cylinder. The jacket has two access lines to allow water to enter and leave the jacket as part of the heat recovery process. All construction is of stainless steel. Because it was desired to maximize safety in this test unit, the vessel construction is much heavier than would be required in a field version of the integrated system. One end of the reactor has a clamped cap, and the other is welded shut. The cap houses a pressure relief valve which opens at 25 psi.

The welded end has several process connections. Hydrogen gas and entrained steam exit through a 1" diameter reinforced hose. At the junction of the hose and the vessel, in the reactor interior, the gas and steam is filtered through a polypropylene filter which can separate particulate matter to 1.1 microns. Additional connections are provided for the entrance of process water, a thermocouple for monitoring temperature in the process water/MAGNIC slurry, and an emergency drain.

Reverse Osmosis Desalination

Reverse osmosis desalination is widely used in commercial and military applications to render brackish water into potable water. In osmosis, two miscible solutions of different concentration will attempt to equalize concentration on either side of a permeable membrane. If the miscible solutions are brackish water and fresh water, fresh water will migrate through the membrane to dilute the salt solution.

Reversing the process produces potable water. By pressurizing the salt water prior to introducing it to a semi-permeable membrane, reverse osmosis occurs. Water in the pressurized salt solution flows to the side with the least pressure. 98% or more of the chloride ion in the brackish water is rejected by the membrane. The low pressure product is potable water.

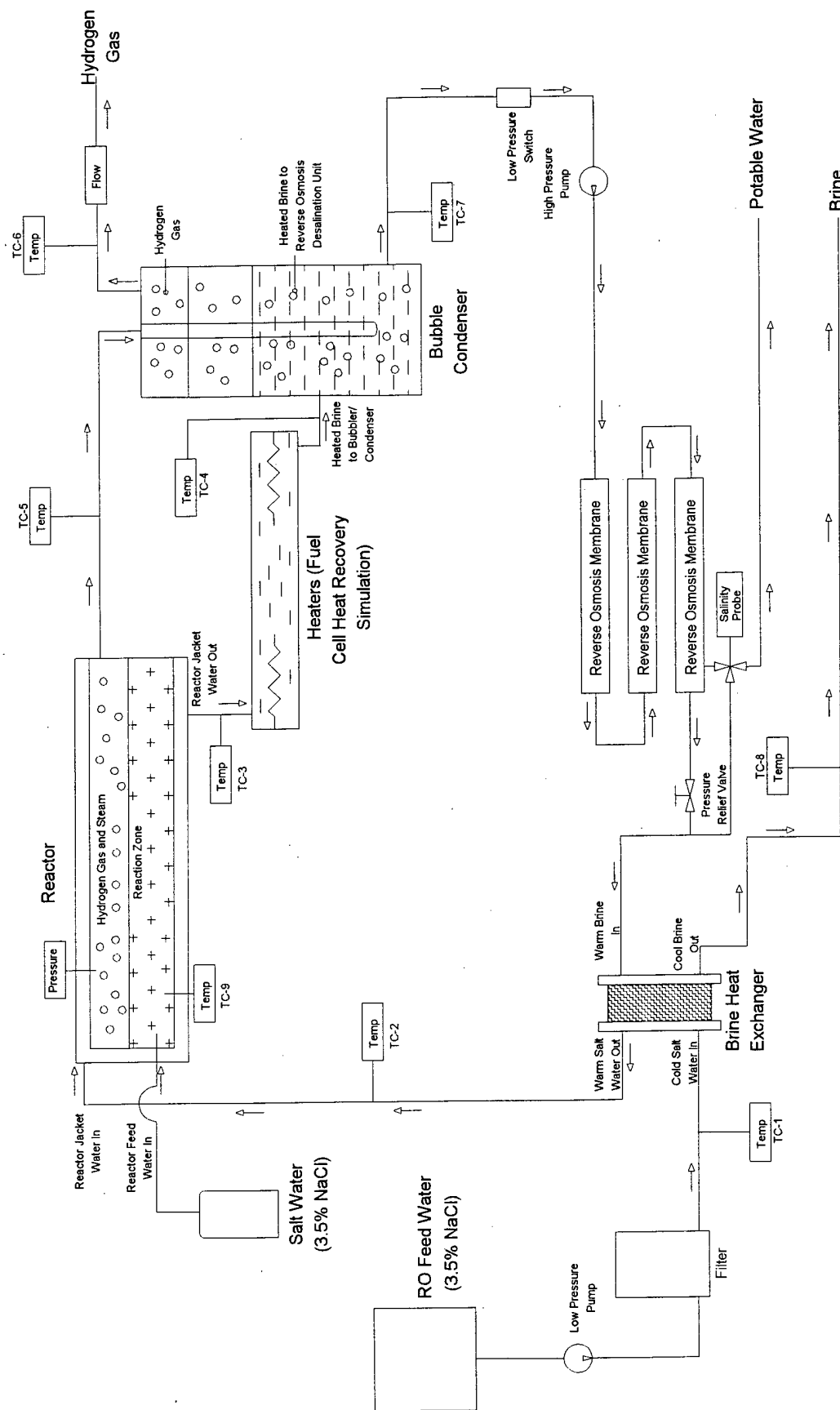


Figure 6. Integrated Demonstration System Flow Diagram

The desalination unit is a commercially available system manufactured by Sea Recovery Corporation. It is capable of producing 600 gallons per day (25 gph) potable water operating under standard conditions (25°C ambient temperature, 3.5% NaCl feed water). The unit centers around three reverse osmosis membranes produced by Dow Filmtec. Dow Filmtec also manufactures the membranes used by the Army in current systems. The membranes used in the skid-mounted unit are high recovery membranes with a minimum chloride ion rejection of 99.2%. In addition to the membranes, the desalination unit consists of three high-pressure membrane housings, a low-pressure pump (10-20 psi), a high-pressure pump (800 psi), filters, a salinity probe, and associated monitoring and safety equipment.

Power consumption by the reverse osmosis desalination unit is largely dictated by pump power consumption. The high-pressure pump is driven by a 1.5 hp motor which has an efficiency of 78.5%. This 230 V, 3 ϕ motor consumes 1.425 kW. The low-pressure pump, which is also 230 V, 3 ϕ , is a ½ hp motor with an efficiency rating of 70%. This motor consumes 0.533 kW. Total system power consumption, including electronics (LEDs, salinity monitoring, and switching) is 2.3 kW (Sea Recovery, 1994.)

Table 4 defines the manufacturer's recommendations for the operation of this unit and lists the weight of a typical 600 gallons per day (gpd) system.

Table 4 . Sea Recovery, Inc SRC600AM ROD Unit Specifications

Parameter	Range or Value
Feed Water Salinity	35,000 -50,000 ppm (3.5-5% NaCl)
Feed Water Temperature	0.5-50°C (33-122°F)
Feed Water pH	3-11
Free Chlorine Tolerance	0.1 ppm
Maximum Input Low Pressure	35 psi
Nominal Membrane Input Pressure	820 psi (3.5% NaCl)
Nominal Feed Water Flow Rate	2.5 gpm
Nominal Weight	150 lbs (68 kg)

The provision of brine to the ROD unit was accomplished with a 150 gallon tank which fed the low pressure pump of the system. This tank contained salt water which was 3.5% NaCl by weight. As the ROD system separated the feed water into concentrated brine and potable water, the brine and water were remixed in the tank. This maintained the salt concentration of the water except for losses due to evaporation. A conductivity meter calibrated for 35,000 ppm NaCl was used to prepare the solution and maintain its concentration to within ± 350 ppm.

Heat Recovery Mechanisms

ROD system function is affected by the temperature of the feed water, as described in Section 2.4 *Effect of Heat on ROD System Performance*. To utilize waste heat, four separate mechanisms were used to recover heat from the MAGNIC hydrogen generation and desalination process. These were a brine heat exchanger, a gas/steam cooling/condensing unit, heat exchange with the reactor vessel, and use of fuel cell waste heat.

As shown in the system schematic representation, water from the brine supply tank was first passed through the brine heat exchanger. The unit consists of layers of radiative heat exchange coils sandwiched between two plates. Cold feed water entering the system circulates through coils adjacent to coils containing warm discharge brine from the ROD. In this way, heat which was already added to the ROD feed water through other processes is partially recovered from the brine and reused. This heat exchanger was used in the feasibility demonstration unit. Extra plates were added for the integrated system. The brine heat exchanger weighs 75 lbs.

Two other methods accomplish more direct heat recovery from the MAGNIC reaction. Feed water leaving the brine heat exchanger is routed through the jacket surrounding the reactor. Heat produced by the exothermic MAGNIC reaction is captured in the MAGNIC/process water slurry in the vessel and transmitted through the jacket walls to the feed water. Also, the gas leaving the MAGNIC reaction was bubbled through feed water passing through a tank.

The tank, called the bubble condenser, consists of an 18 gallon polypropylene tank with a pipe that enters in the top of the unit. This pipe was attached to the 1" diameter reinforced hose exiting the reactor vessel. The pipe has a customized tip which breaks the gas and entrained steam into bubbles. Hydrogen gas rising from the feed water exits via a port on the top of the bubble condenser. ROD feed water enters through a port on the upper side of the tank, and exits through a port near the bottom. At 12" diameter and 36" in height, the bubble condenser was oversized for experimental reasons.

Bubbling product gas through feed water was intended to have two effects. First, hydrogen gas which was leaving the zone of the reaction has picked up heat. Gas bubbling through the feed water loses its heat. Second, steam which was entrained with the gas condenses into the tank feed water. Any impurities which were not captured by the vessel filter remain in the tank, and are not passed through to the PEM fuel cell. These impurities are not a significant source of contamination or fouling in the ROD system, so their presence in the feed water is not an operational concern.

The fourth heat recovery mechanism was utilization of fuel cell waste heat. No affordable fuel cell was found for the demonstration unit. To simulate waste heat recovery, feed water was passed through a 3" stainless-steel pipe. Two Chromolux immersion heaters were placed in the ends of the pipe. Reducing couplings connect the heaters to the ends of the pipe. Welded fittings on the pipe provide for the water inlet and outlet. The immersion heaters are rated at 2 kW each.

At 50% efficiency, the fuel cell was calculated to produce 3.04 kW of electrical energy from 2 kg of MAGNIC. The remaining 50% of the energy available from the hydrogen gas appears as waste heat from the fuel cell. Hence, approximately 3 kW of heat was available. In one of the heating elements, a Variac reduced the input voltage and hence the output power of one of the heaters to 470 W. This is done on the assumption that the method of heat exchange between the fuel cell and the brine fed to the desalination plant is only 80% efficient. Hence, if the reactor is 50% efficient, then the total heat transferred to the brine is $0.5 \times 0.8 \times 6.08 \text{ kW} \approx 2.43 \text{ kW}$. For a ROD feed water flow rate of 2.5 gpm, 2.43 kW of power can raise the temperature of the water by 3.7°C.

Heat recovery from the brine heat exchanger is demonstrated in Figure 7. The dashed line represents water input from the brine tank to the inlet side of the brine heat exchanger. The solid line is water exiting the heat exchanger prior to entering the reactor jacket. Initially, as water circulated through the system, the temperature of the water dropped to reflect the injection of cooler water from the brine tank. Water entering and exiting the heat exchanger remained close in temperature until other heat recovery methods began to add heat to the ROD feed water. As the feed water temperature began to climb, warm brine in the opposite side of the exchanger began to add heat to the jacket inlet water. From the time that the system began to exhibit increased brine temperature due to heat recovery, the brine heat exchanger added an average of 5.7°C to the ROD feed water temperature.

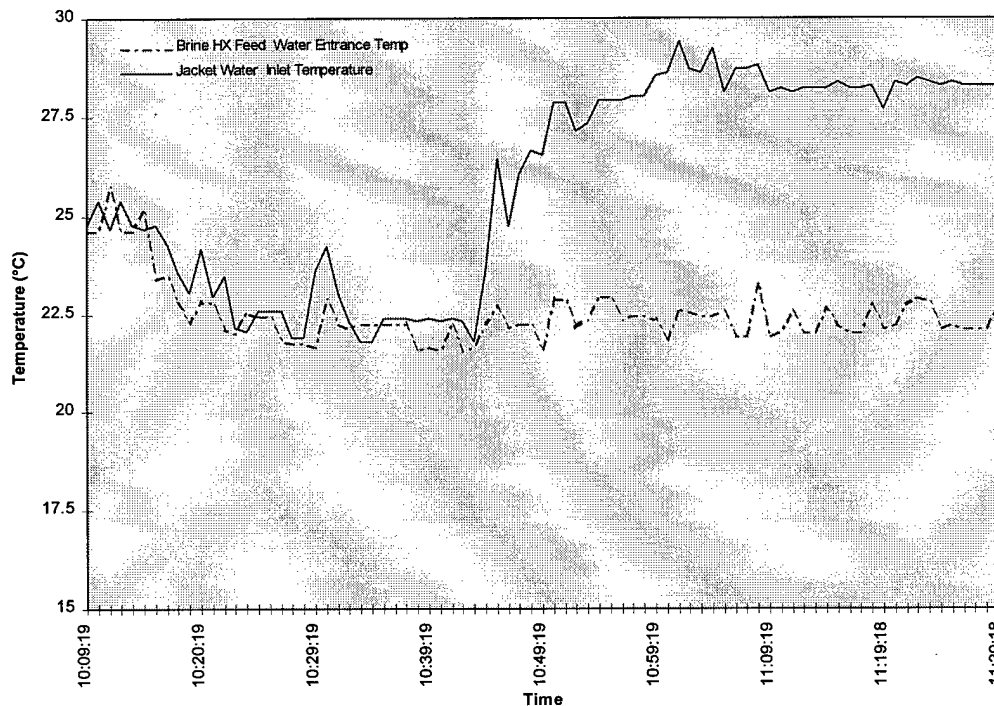


Figure 7. Brine Heat Exchanger Feed Water Temperature Effect

Heat recovery directly from the MAGNIC reaction via the reactor vessel water jacket is illustrated in Figure 8. The dashed line represents the jacket water inlet temperature. This water has already been heated by the brine heat exchanger, and is picking up additional heat from the reaction via heat conduction from the stainless-steel vessel. The average heat recovered from the reaction over the indicated time interval is 7.4°C.

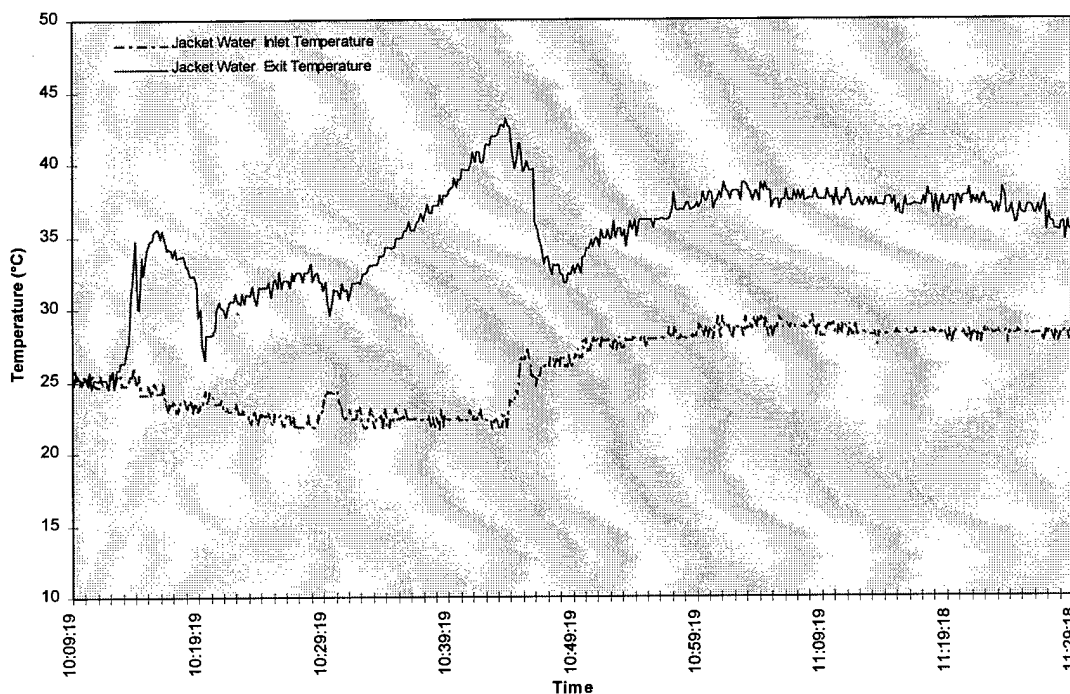


Figure 8. Reactor Jacket Heat Recovery Effect

Prior to entering the bubble condenser, additional heat for a period of the system operation was picked up from the simulated fuel cell heat recovery unit. Figure 9 illustrates the operation of the simulated heat recovery unit. The unit was operated for only a brief period of time, because the feed water heat from all sources was approaching a value which was unsafe for the ROD system. This topic is addressed in greater detail in Section 2.4 *Effect of Heat on ROD System Performance*. In the time interval shown, the heater added 2.8°C to the ROD feed water.

Figure 10 is a plot of the heat recovery from hydrogen gas and steam passed through the bubble condenser. The dashed line represents ROD feed water pumped through the bubble condenser. This water has already picked up heat from the brine heat exchanger and from the reactor jacket. Some additional heat was picked up from the simulated recovery of heat from the fuel cell. As seen, the bubble condenser initially removed heat from the system. The inlet water temperature profile is synonymous with the exit temperature of the reactor jacket.

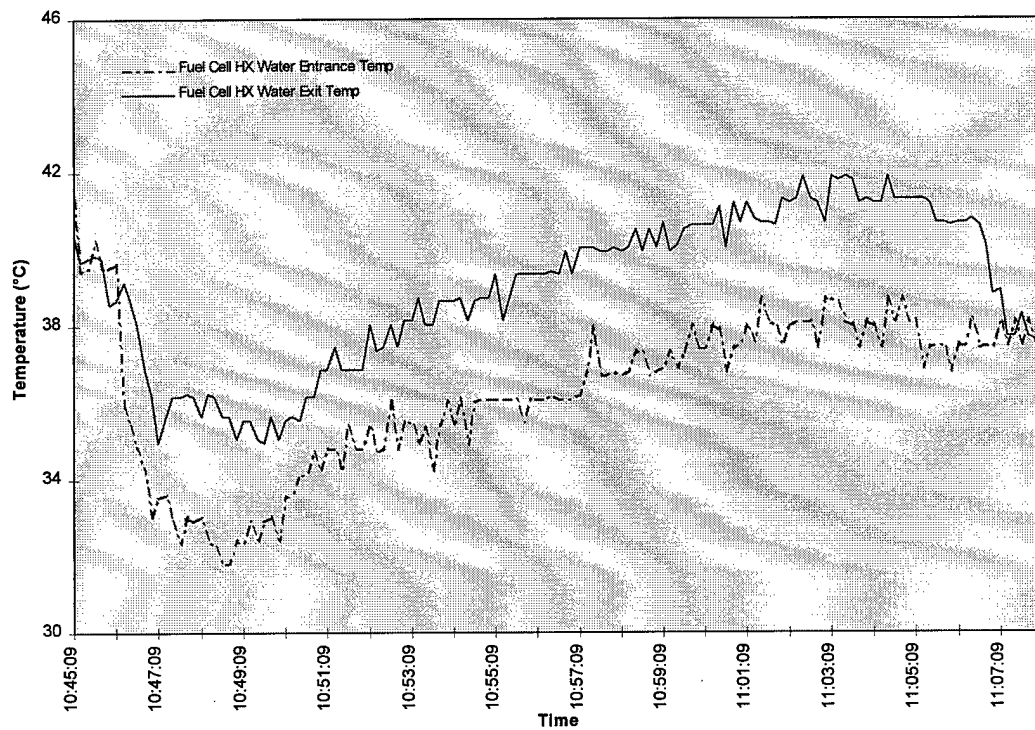


Figure 9. Fuel Cell Simulated Heat Recovery Effect

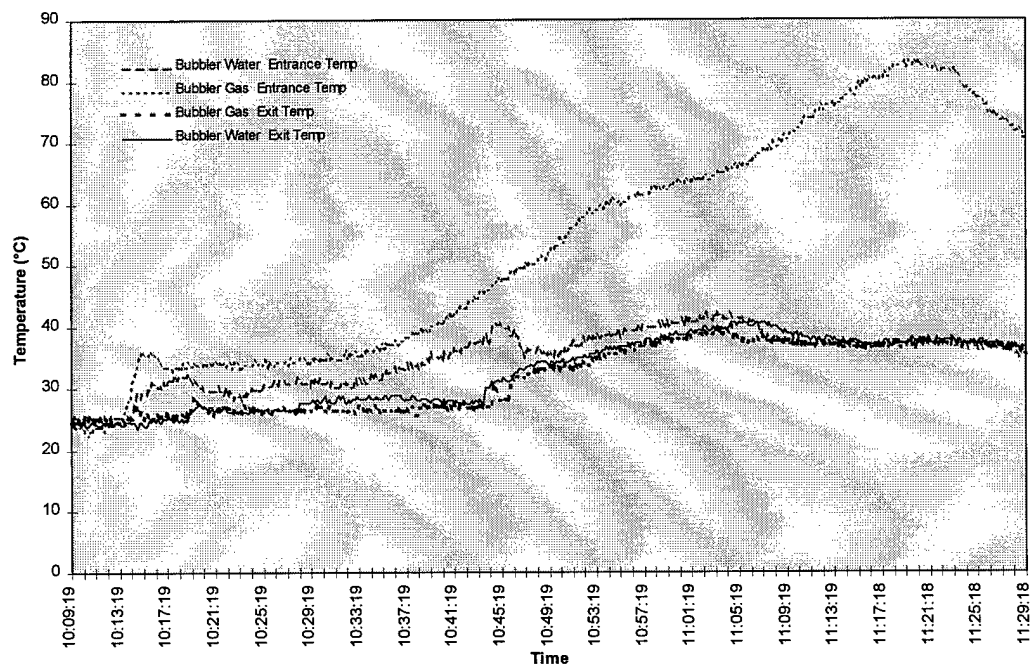


Figure 10. Bubble Condenser Gas and Feed Water Temperature Effect

The bubble condenser contained an initial volume of water. The incoming water, carrying heat from the prior heat exchange methods, lost heat to the mass of water already in the tank. Much of the reaction time period was spent in bringing the inlet and exit water to equilibrium with each other. Although hydrogen gas and steam were bubbling through the tank, no significant amount of heat was added to the water from the condensation of reaction steam or from gas. However, the bubble condenser did function to remove heat from the incoming gas. Saturated gas at temperatures as high as 83°C was cooled to the bubble condenser water exit temperature.

The photographs of Figures 11 and 12 show the assembled unit. In Figure 11, the components of the integrated system, identified counterclockwise from the bottom left of the skid, or leave, the bubble condenser, the high pressure pump, the brine heat exchanger (flat plates at bottom right, fins are sandwiched between plates), the reverse osmosis desalination unit high-pressure housings, the temperature/pressure indicators and heater control panel, the desalination unit control panel, and the main power disconnect. The low-pressure pump is in the rear of the skid behind the reverse osmosis desalination unit high-pressure housings.

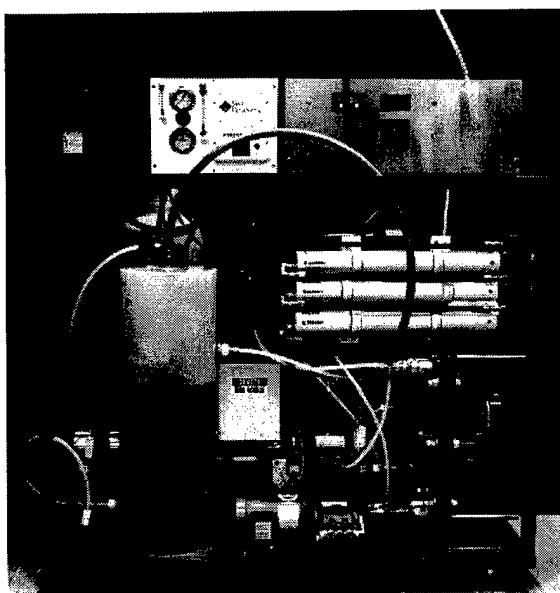


Figure 11. Integrated System-Front View

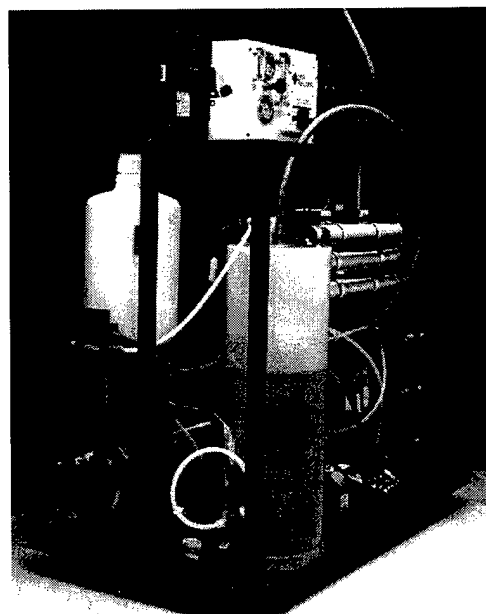


Figure 12. Integrated System-End View

2.4 Effect of Heat On ROD System Performance

ROD Membrane Porosity

The thin-film membranes of the ROD system exhibit increased porosity with increasing temperature. Figure 13 shows the change in water flux through a membrane as a function of temperature.

Figure 13 also illustrates the theoretical effect of temperature on salt rejection. As pointed out in Section 2.3 *Design and Construction of Integrated Demonstration Unit*, modern ROD membranes have typical salt rejection (chloride ion) of greater than 99%. As indicated by Figure 13, rejection decreases only slightly, even at elevated temperatures. At 50°C, which is the maximum allowable temperature for ROD membrane operation, chloride ion rejection is still 98.9%.

The increased porosity of the ROD system membrane at elevated temperatures implied that waste heat from the MAGNIC reaction could be used to produce the system nominal production rate of 25 gph with less pressure on the feed water input to the membranes. Alternatively, it should also be possible to increase gph throughput while maintaining nominal feed water input pressure (820 psi for 3.5% NaCl feed water.)

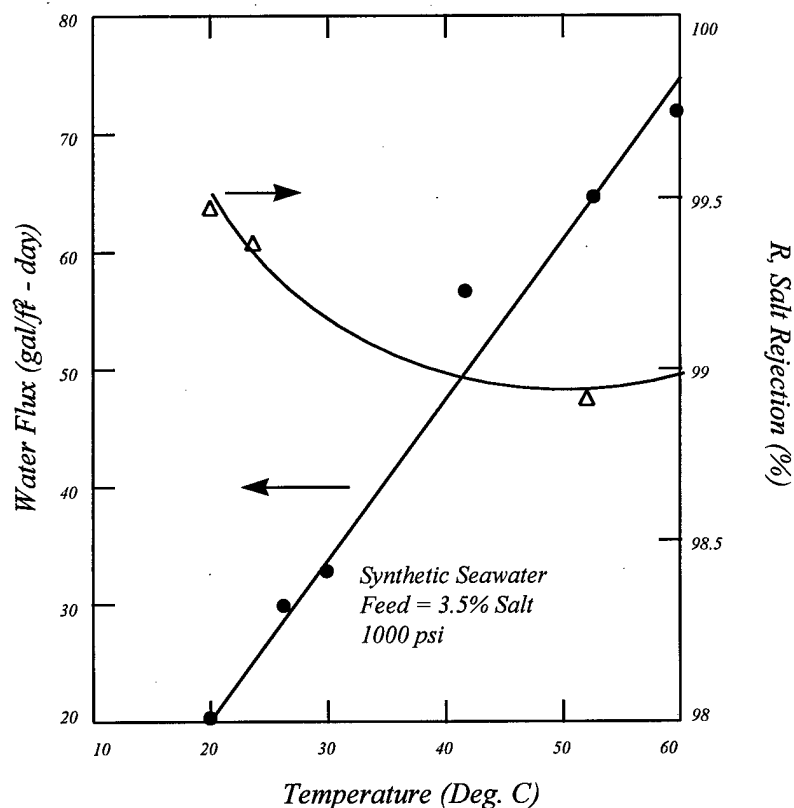


Figure 13. Temperature Effects on ROD Membrane Performance

Laboratory Tests of Reduced Power/Increased Flux Hypothesis

Initial laboratory tests of the effects of added waste heat on ROD membrane performance demonstrated a reduction in pump input power as ROD feed water temperature increased. The experimental results from one such test are shown in Figure 14. 3.5% NaCl salt water at an initial temperature of 17°C was heated and fed to the ROD system. The input power was monitored with a three phase power analyzer as the water temperature increased to 32°C. The system was maintained at a constant output of 25 gph by adjusting the system pressure manually. As the figure shows, an increase in ROD feed water of 15.2°C will reduce pump power consumption by 8% while maintaining potable water production between 24.5 and 25 gph.

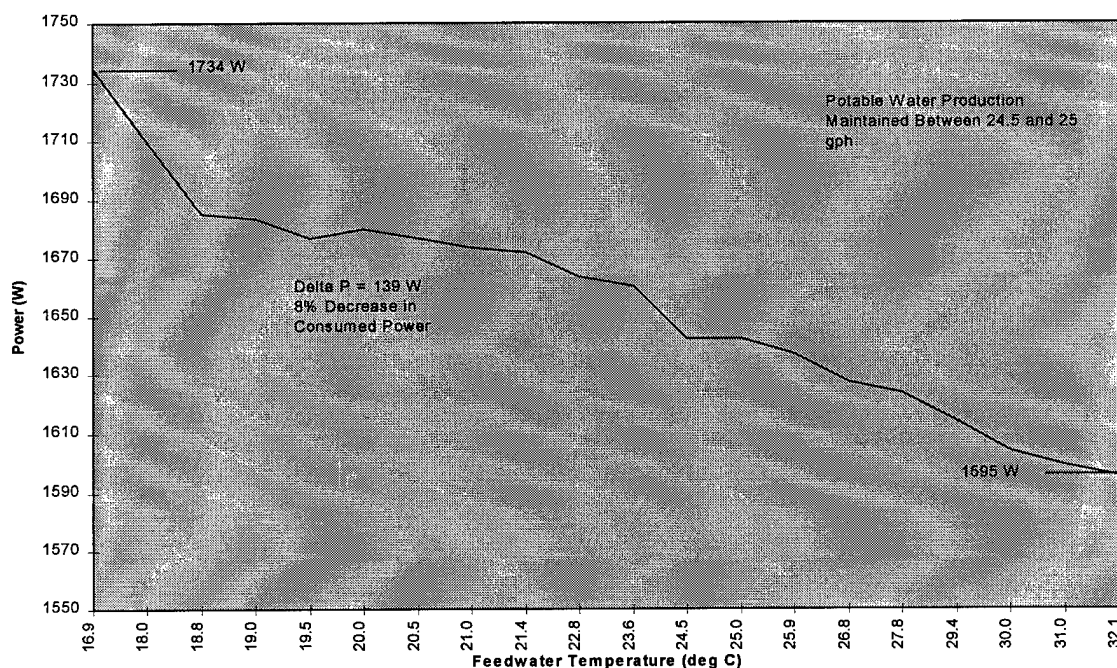


Figure 14. Consumed Power as a Function of Reverse Osmosis Feed Water Temperature

The relationship between power reduction and feed water temperature can be reasonably well described by a linear function, with temperature T (°C) as the independent variable.

$$Power = -6.2T + 1720$$

If feed water temperature were increased to the maximum value of 42°C, based on the energy recoverable from the reaction, the final input power would have been 1460 W, which would have been a 15.8% reduction of input power.

Feed water temperature was not increased to the maximum obtainable temperature because the response of the ROD membranes to water at temperatures above 36°C was not as predicted by the manufacturer. Although the system was operated in a manner consistent with the manufacturer's recommendations, it was observed that the salt rejection ability of the membranes was reduced markedly as temperatures approached 36°C. Ideally, the commercial system rejects all water with a salt concentration of greater than 1000 ppm. This is a reasonable standard from a human health and safety point of view. (World Health Organization standards are 500 ppm. In some arid environments, where "fresh" water is brackish, it is normal to find water with concentrations as high as 1500 ppm.)

Simulations run with the Reverse Osmosis System Analysis (ROSA) software provided by Dow Filmtec suggested that salt rejection should be functioning even at the maximum operating temperatures. However, consultation with Dow Filmtec and Sea Recovery, Inc. indicated that there is a manufacturing tolerance for the membranes of $\pm 15\%$. Possibly a combination of tolerances in the salinity sensing system, combined with the membrane tolerance, traces of storage chemicals which were not completely flushed, and/or other factors led to this behavior. Although the reasons for the behavior of the commercial system are not clear, the research team believes that the figure of 15.8% reduction in power should be generally achievable within the limits of commercially produced membranes.

The ROSA software does support the occurrence of reduced pressure for constant potable water production rates as temperature increases. This behavior is shown in Figure 15 for a simulated membrane.

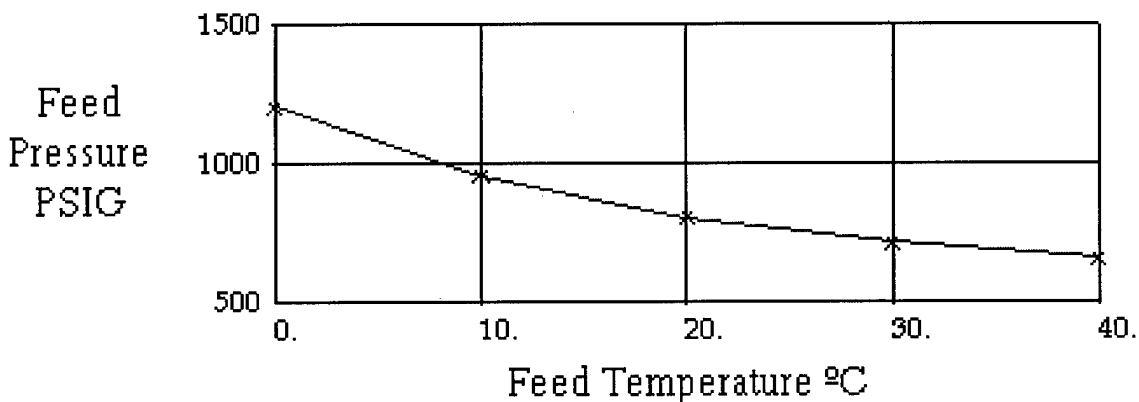


Figure 15. Simulated Feed Water Pressure vs. Feed Water Temperature for a Reverse Osmosis Membrane

2.5 Characteristics of the MAGNIC Reaction

Several experiments were run with the integrated system to examine the behavior of the MAGNIC reaction as compared with the bench-scale reactor. Experiments were performed which investigated the effect of pre-heating of the process water, both by use of mixed fuel geometries (e.g., flakes and plates), and by utilizing heated source water. The kinetic effect of different reaction geometries under similar conditions was noted.

Reaction Rates

The rate of reaction of magnesium in the presence of salt is primarily dependent upon process water temperature and the amount of exposed surface area available to the process water. Because exposed surface area is critical, much work was performed in Russia on developing a process which provided maximum surface area. In the course of this work, several metal additives were investigated as potential accelerators of the magnesium reaction process. It was found that nickel alloyed with magnesium in concentrations of 1%-2% significantly enhanced the process. The addition of nickel contributed to the phenomenon of pitting in the surface of the MAGNIC alloy, as compared to pure magnesium. The profusion and increased depth of metal pits appears to offer much greater surface area for the formation of hydrogen gas from the reaction. The electrochemistry of this reaction was investigated in a report to the Army in the early stages of this project. (Myers, et.al., 1996)

Like most metals, the MAGNIC alloy will form a surface oxide layer upon exposure to air. The formation of the oxide layer is beneficial to the stable storage of MAGNIC. As in the formation of aluminum oxides, the oxide layer inhibits further reaction, forming a protective coat on the alloy surface. However, in the MAGNIC reaction, this oxide layer must be dissolved to expose surface area of the MAGNIC to the process water. Figure 16 is a comparison of flow rates for two experiments which illustrates this point.

One experiment used rods which were coated with an oxide layer from prolonged exposure to air. 2 kg of the rods were distributed evenly in the bottom of the reactor. 75 grams of MAGNIC flakes contained in small bags were distributed at even intervals throughout the reactor as well. Another experiment used plates machined from ingots, with an average thickness of 7 mm. No flakes or other geometries were used in the experiment with plates. The machined surfaces of the plates were not covered with a noticeable oxide layer. The experiment used approximately 2 kg of MAGNIC plates.

Initially, the experiment utilizing rods and flakes produces more hydrogen. There is a burst of hydrogen as the flakes, which are machine tailings and have oxide-free surfaces, react with the salt water. The reaction then subsides to a steadily increasing production rate. Initial production surpasses the plate reaction, but as the flakes are consumed, the reaction rate slows considerably. By contrast, the plate reaction begins steadily increasing, with the plates producing hydrogen at more than twice the rate of production of the rods.

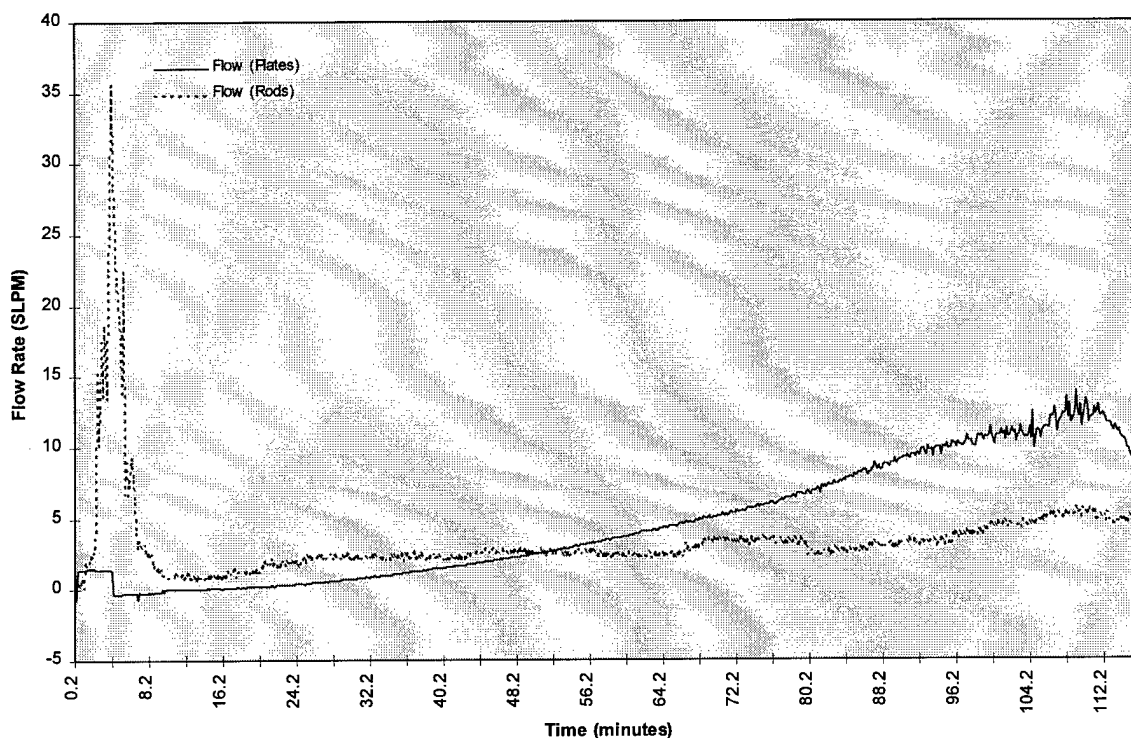


Figure 16. Effect of Surface Oxidation on MAGNIC Reaction Rate

The rate of reaction of the plates is aided by the increased heat available to the reaction. In the experiment with plates, 13 liters of 3.5% NaCl were used (4.3x stoichiometric water). Only 9.4 liters of 3.5% NaCl solution were used with the rods (3.1x stoichiometric.) The plate experiment exhibited a temperature increase of 47°C in the process water. The rod and flake experiment only contributed a 25°C increase to the process water temperature over a comparable interval, even though less water was used. The evidence suggests that oxide from air or water exposure would inhibit the reaction until the oxide layer had been removed by reaction with the NaCl solution. Once the oxide layer is dissolved, the reaction proceeds at a rate determined by the fuel geometry (surface area) and the temperature.

The use of flakes was suggested from previous experiments in the bench-scale reactor as a possible method of accelerating the MAGNIC reaction in the integrated system. Until boiling conditions are reached, reaction heat energy is expended in heating water. Additional heat in the process water from the rapid oxidation of MAGNIC flakes or dust in salt water should decrease the time needed for the process water to reach boiling point.

This concept was tested experimentally using mixed flakes and dust from machining operations on MAGNIC ingots. In this experiment, the flow of water through the reactor jacket (as a heat

exchange mechanism) was suspended. 14.2 liters of 3.5% NaCl water at an initial temperature of 34.4°C were added to the reactor. To create the effects of fuel mass, the water was intended to replace the mass of 2 kg of plates, 4x stoichiometric water for 2 kg, and 3.3x stoichiometric water for the flakes and dust. Figure 17 shows the effect on the process water temperature of the oxidation of 200 g of MAGNIC composed of 160 g of flakes and 40 g of dust.

The delay between the addition of process water and the registration of the water temperature is the length of time required for water in the reactor vessel to reach the thermocouple, which is suspended above the bottom of the vessel. At that point, the temperature is observed to rise rapidly, first to the temperature of the process water, then to a maximum value as the MAGNIC reaction proceeds rapidly due to the large exposed surface area of the flakes and dust. The process water reached a peak temperature slightly in excess of 55°C in 7 minutes. At this point, the flakes and dust had reacted to completion, and the process water began to rapidly lose temperature due to the mass of the reactor and the mass of water in the reactor jacket.

A second experiment was performed with 400 g of MAGNIC composed of 237 grams of flakes and 163 grams of dust. This experiment also used zero jacket water flow. 15.4 liters of 3.5% NaCl water at an initial temperature of 34.4°C was prepared for addition to the reactor. The water replaced the mass of 2 kg of plates, 4x stoichiometric water for 2 kg, and 2.5x stoichiometric water for the flakes and dust. Figure 18 shows the effect on the process water temperature.

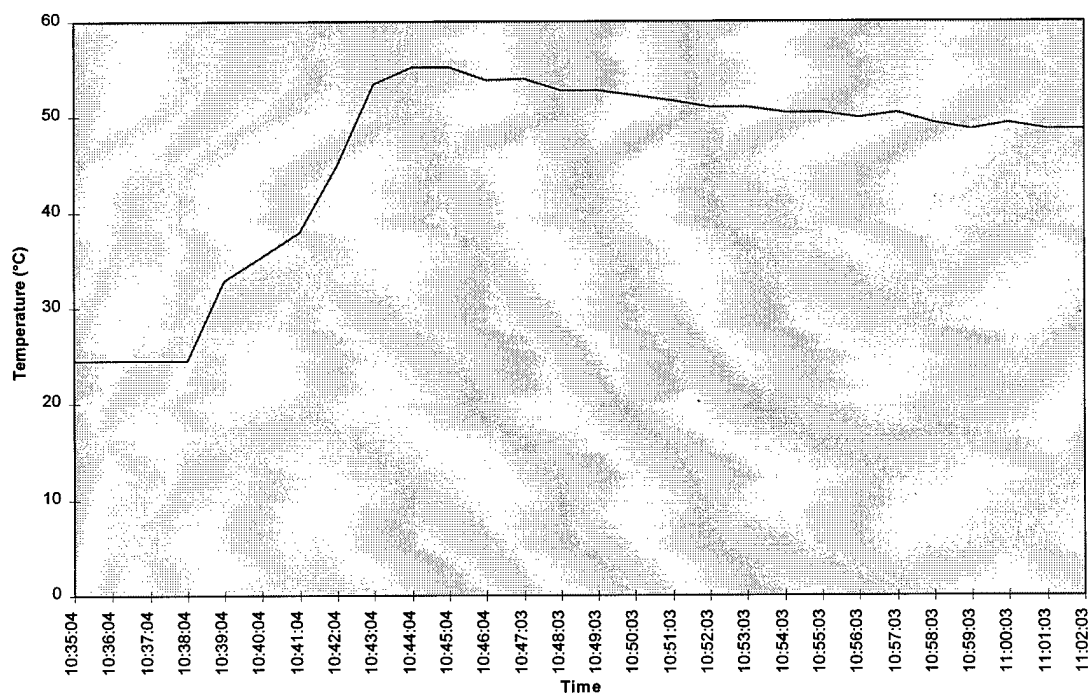


Figure 17. Effect of Flakes on Process water Temperature

Initially, the reaction followed the path of the earlier experiment. However, at about 5 minutes into the experiment, the rapid oxidation of the flakes and dust created a high rate of production of hydrogen, and excess hydrogen began to flow into the process water container. The addition of process water was suspended and flow of water through the jacket was established to carry heat away from the reaction. Process water was reintroduced to the vessel after the surge of gas had subsided. However, the reaction had gone to completion in about 10 liters of water, raising the temperature of the water to nearly 74°C in 7 minutes. Upon removal of the tray from the reactor vessel, rapid boiling in the process water was found to have caused foaming or frothing of the byproduct. This spreads the byproduct throughout the vessel, and coats the filter, which inhibits the passage of gas and steam through the filter.

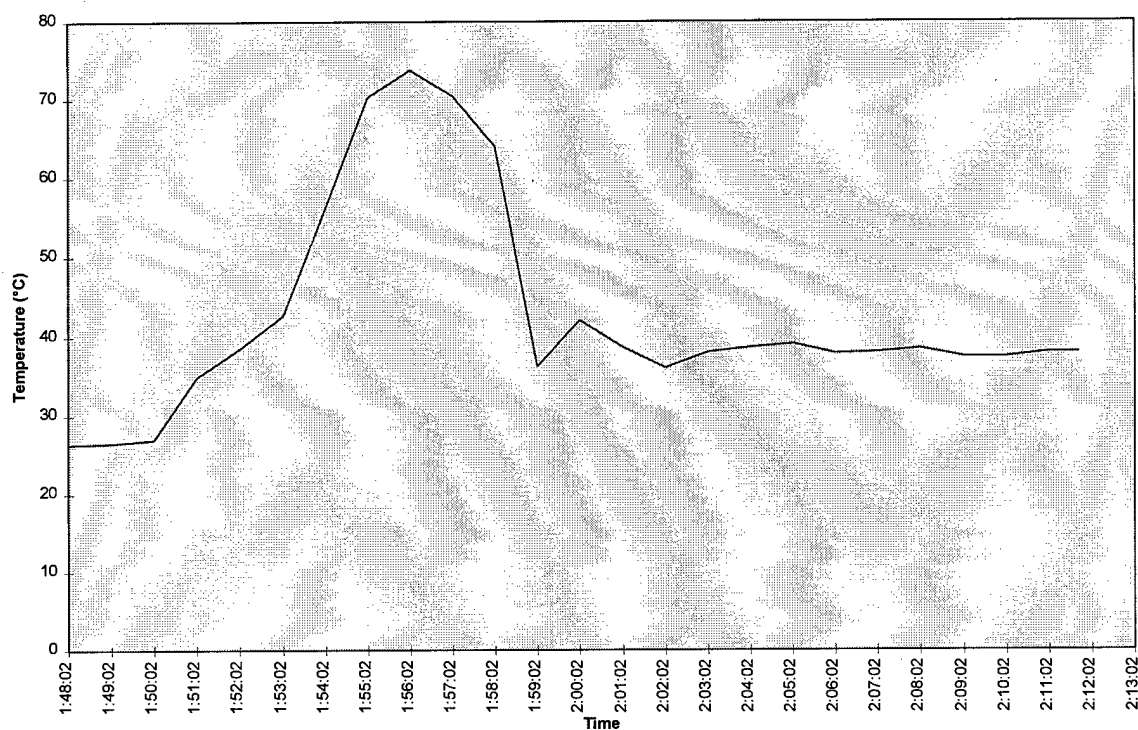


Figure 18. Effect of Flakes on Process water Temperature

In Figure 16, the flakes produced a high rate of change in the gas flow. However, with water flowing through the reactor jacket, any heat contributed was quickly lost to the cool mass of the reactor vessel. In the experiment of Figure 17, absence of jacket water flow undoubtedly

contributed to the sustained increase in process water temperature. For sustained temperatures, the temperature difference which must be overcome by the MAGNIC reaction to reach maximum hydrogen production rates could be reduced by at least 25°C, depending on the incoming process water temperature. As the second flake experiment indicates, addition of a larger amount of fine particles can reduce the temperature barrier even more. An optimum amount would have to be determined for a given charge to prevent frothing. In the presence of jacket water flow, the heat produced would be quickly removed. This problem could be solved by monitoring the heat of the jacket water and only establishing flow when the jacket water temperature was near the limitations of the ROD system.

The positive effect of process water temperature on reaction speed was established in experiments which used pre-heated process water. The effect is illustrated by the experimental results shown in Figure 19. The reactor was loaded with approximately 2 kg of plates. 5x stoichiometric water heated to an initial temperature of 65.9°C was used for the experiment. The reactor jacket was pre-heated to 58°C to reduce loss of heat to the vessel and jacket water.

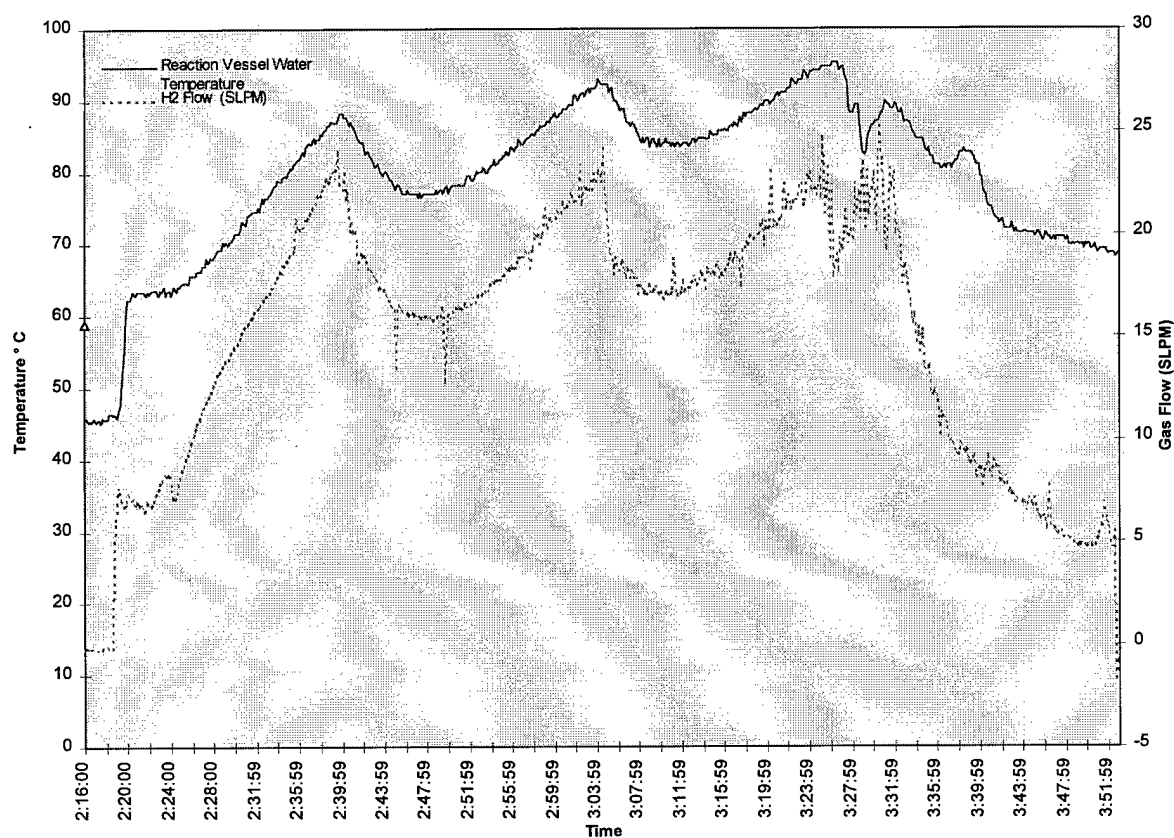


Figure 19. Effect of Pre-heated Process water on Kinetics of MAGNIC Reaction

The majority of experiments which utilize process water at nominal temperatures (25°C or less) required over an hour for the process water to reach 90°C . In contrast, this particular experiment required only 23 minutes to reach a peak temperature of 88°C .

The flow of gas and the increase in process water temperature due to the exothermic reaction are interrupted because of the need to periodically establish jacket flow to reduce exit gas temperature. The mass flow meter monitoring the experiment is intolerant of moisture. Although a copper condenser coil and a desiccant trap were used to reduce water in the gas stream, when the gas temperature exiting the reactor approached 90°C at high rates of flow (12 SLPM or greater), the condenser and desiccant could not be relied upon to remove water quickly and thoroughly enough to prevent damage to the meter. This is the cause of the peaks and valleys in the temperature and flow rate curve of Figure 19.

The preheating of the reactor jacket also has measurable effect on the length of time required to establish the maximum water temperature, and hence maximum gas flow. This is illustrated by Figure 20. In this illustration, data from two experiments are compared. Both experiments

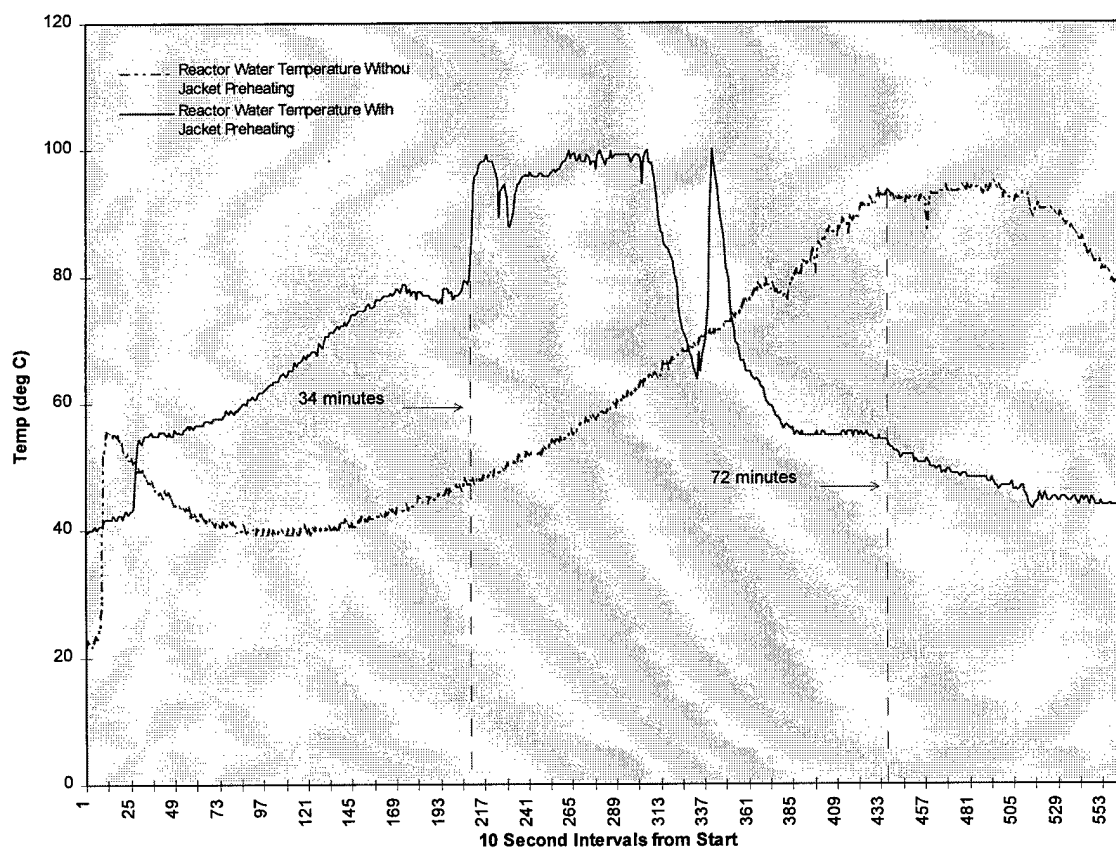


Figure 20. Comparison of Reaction Time With and Without Vessel Pre-heating

utilized approximately 1 kg of plates and 6 liters of 3.5% NaCl process water. In one experiment, the process water was heated to 60.6°C. The jacket was not preheated, and the mass of jacket water and the vessel was at room temperature. In the other, the jacket water was preheated to 57.4°C. Process water initial temperature was 57.1°C. The initial internal surface temperature of the reactor vessel was measured to be 48°C before loading the MAGNIC plates. Jacket water flow was initially suspended in both cases. The prevention of heat loss to the mass of water in the reactor jacket and in the mass of the reactor vessel reduced the time for peak process water temperature by $\frac{1}{2}$.

Post-reaction temperature loss in the mass of reacted by-product is slow in the absence of water flow. Tests show a minimum of two hours for the byproduct mass to lose 20°C of heat to a room where ambient temperature was 25°C or less. In hot environments (e.g., desert or tropical) the time to cool from maximum reaction temperature to 45°C would be several hours. This creates a challenge to recharging the unit. However, as the above experiments indicate, it would be to the advantage of the reaction to be able to load MAGNIC fuel into a heated system.

To minimize the impact of the temperature on the personnel managing the unit, and take advantage of the stored heat in the vessel, a cartridge loading system could be developed which contained the post-reaction byproduct and the excess process water. This cartridge could be removed from the container using tools designed for the purpose, and left exposed to cool while a new cartridge was loaded into the vessel. Since the byproduct is non-toxic, exposure risk is associated only with heat. The cartridge can incorporate filtration to minimize reloading time and cleaning. Cartridges would be recyclable to recover $\text{Mg}(\text{OH})_2$ by-product for commercial use and/or to reload with a new charge of MAGNIC.

2.6 Field Operation Characteristics

Use of the MAGNIC reaction for desalination in the field requires that its physical attributes support the Army mission. Deployment of the unit is facilitated by a light weight, small footprint system. For a given size, the system must have a high ratio of mass/rate of potable water produced to total system mass. In addition, in the face of ever-shrinking budgets, a system that minimizes Army investment is desirable. Although not stressed by the Army, an easily concealed device with low heat and audible signature is a plus in field operations.

Mass Efficiency

Previous descriptions of the MAGNIC integrated system relied upon the concept of *mass efficiency*. Mass efficiency was defined as the ratio of potable water produced in gallons per hour to system weight in pounds. The mass efficiency of the MAGNIC system was determined in relation to the existing Army diesel powered desalination unit (660 gpd). Mass efficiency was also determined for different configurations of the MAGNIC integrated system. The system was considered without heat recovery, with heat recovery, and as an weight-optimized system

using heat recovery to obtain maximum ROD system throughput.

Without heat recovery, the mass efficiency of the integrated system is comparable to the diesel unit. As described in Section 2.4 *Effect of Heat on ROD System Performance*, throughput of the ROD system membranes theoretically increases as a function of feed water temperature. For a rise in temperature of 13°C in the ROD feed water, the mass efficiency of the integrated system improves by 29%. If the integrated system is optimized by reducing the weight of the heat exchange components (by eliminating brine heat exchange and optimizing the weight of the reactor and bubble condenser), the mass efficiency improves by nearly 44% over the integrated system without heat exchange. Table 5 defines the weights and mass efficiencies of the compared systems.

Table 5 calculations were performed based on the theoretical determination of the heat recoverable from the reaction by the various heat exchange methods. These calculations indicated that the contribution of the brine heat exchanger to heat recovery were not sufficient to overcome the penalty associated with its weight. The assumed flow rates in this system were higher than are actually in use, which led to underestimation of the heat recovery. As shown in Section 2.3 *Design and Construction of Integrated Demonstration Unit*, empirical data indicated that the brine heat exchanger allowed significant heat recovery from the discharge brine. In light of this improvement, the small amount of heat (essentially zero) recoverable from the bubble condenser did not offset its mass penalty in the system.

The throughput increase of the ROD membranes based on increasing porosity at elevated temperatures is a documented effect. However, from a practical standpoint, operating the ROD membranes at higher than their nominal rate of production (25 gph) can lead to membrane

Table 5. System Weights and Mass Efficiencies without Brine Heat Exchange

Unit	Description	Weight (lbs)	Major Equipment	Water Production (gal/hr)	Mass Efficiency (gal/lb)
1	Diesel Desalination Unit	450	Diesel Generator (150 lbs)	25	.056
2	MAGNIC (non-optimized) without heat exchange	440	Reactor (70 lbs) Fuel cell (120 lbs)	25	.057
3	MAGNIC (non-optimized) with heat exchange ¹	470	Reactor (70 lbs) Fuel cell (120 lbs) Heat exchange (30 lbs)	34.8	.074
4	MAGNIC (optimized) with heat exchange ¹	425	Reactor (45 lbs) Fuel cell (120 lbs) Heat exchange (30 lbs)	34.8	.082

1. Heat exchange consists of recovery from reactor jacket, fuel cell heat exchange, and bubble condenser

deterioration and salinity problems. As documented above, the production of potable water at the rate of 25 gph can be accomplished with reduced input pressure, and hence reduced input power. To provide a comparison between the different systems which is supported by experimental data, reduced system weight was related to reduced steady-state input power requirements. Also, to create an appropriate unitless number for the mass efficiency, the meaning was changed from ratio of gallons of potable water per hour to system weight in pounds to pounds of potable water per hour to system weight in pounds.

The total heat recoverable from the reaction of 2 kg of MAGNIC is 7000 kcal. For a flow rate of 150 gph, the rise in temperature attributable to 7000 kcal of heat is 12.3°C. Based on experimental data (see Section 2.4 *Effects of Heat on ROD System Performance*), the recovery of heat from the reactor is 60% efficient. From experimental data, the brine heat exchanger recovers 78% of this heat for use by the ROD feed water. The ROD feed water collects 5.7°C from the discharge brine. Experimentally, total heat added to the feed water from the brine heat exchanger and the reactor jacket is 13.1°C. Combined with the theoretical increase of 3.7°C available from the fuel cell simulated heat recovery, the total temperature rise in the system is nearly 17°C.

As seen from experimental results in Section 2.4, the reduction of input power is a linear function of temperature. For an increase in feed water temperature of 17°C, the pump input power can be reduced to 1460 W, which is a reduction of 15.8% in input power. Since the fixed power requirement of the ROD system electronics is 342 W (2.3 kW minus nominal pump power requirement), the total power requirement is 1802 W.

At steady-state conditions, the amount of MAGNIC required to produce 1802 W is 1.1 kg. This is slightly more than a third of the fuel weight design requirement for the skid reactor. If all other dimensions were preserved, the reactor volume could be reduced by 63%, with a corresponding reduction in weight. Since the reactor weighs 60 lbs, a steady-state reactor for the system would weigh only 22 lbs, even if constructed of 316L stainless steel at current over-designed safety factors.

For a system which does not utilize heat recovery, the reactor is required to produce hydrogen to provide 2.3 kW of power. This can be accomplished with 1.4 kg of MAGNIC. This reduces the reactor volume by 53%, which results in a non-optimized reactor weight of 31.8 lbs.

As the previous work has indicated, the MAGNIC system weight can be reduced. The integrated system was overdesigned for experimental and safety reasons. In particular, use of light materials in a system designed for atmospheric pressure could cut the weight of some portions of the system by 50% or more.

Choice of materials for an optimum weight system are driven by the need for heat tolerance, thermal conductivity for heat exchange, and tolerance of moderately alkaline solutions. Several options exist for reactor design and construction. The reactor could be constructed of a non-

reactive metal such as titanium. Alternatively, construction could employ a plastic or even suitably protected glass. Another option is to use aluminum which is lined with a non-reactive coating. Coating candidates include various epoxy plastics, CTFE (a fluoropolymer), phenylene oxide plastics, or polysulfone plastics. All of these plastics have the necessary resistance to alkaline materials. All can withstand the nominal reaction temperature of 100°C.

For example, suppose that a reactor were constructed of titanium. The steady-state reactor vessel is constructed of 316L stainless steel. Titanium is 44% less dense than 316L stainless steel, implying that even with safety factors used in the integrated system, the reactor weight could be reduced from 22 lbs to approximately 12.3 lbs. The bulk of the current weight of the brine heat exchanger derives from the use of the steel plates which sandwich the steel cooling fins. A cheaper and lighter unit based on the same design would employ aluminum plates and fins. The brine heat exchanger could be reduced to 26 lbs from aluminum construction.

Previous estimates of fuel cell weights have also been updated to reflect newer PEM devices composed of stackable modules. A commercially available 3.5 kW PEM fuel cell weighs 35 pounds. The minimum input power requirement, regardless of the use of heat recovery, will always be 2.3 kW. This reflects the need to start the ROD system from a "cold" MAGNIC system condition. The weight of the fuel cell can be estimated proportionally at 25 lbs.

Using these numbers as the basis for an optimum-weight MAGNIC integrated system, and comparing these systems (based on the steady-state energy requirement) to the diesel-based unit results in the mass efficiencies shown in Table 6. A graphical representation of the mass efficiency of these systems is shown in Figure 21.

As can be seen from Figure 21, the use of the MAGNIC system for ROD desalination exhibits favorable mass efficiency characteristics when compared to the diesel-based ROD unit. Without the use of heat exchange, the reduction in mass from replacing the diesel generator with an appropriately sized fuel cell and reactor offers a 40% increase in mass efficiency.

The addition of heat exchange, using an appropriately sized fuel cell and reactor without optimizing component weights, reduces the gain considerably. However, this system is still 13% more mass efficient than the diesel based unit. Optimizing the system weight at steady-state power conditions offers approximately the same gains as the MAGNIC-powered system without heat recovery. However, the weight-optimized system is marginally less mass efficient.

Earlier estimates placing the weight-optimized MAGNIC system at an advantage relative to diesel and non-optimized MAGNIC relied upon the increased membrane throughput. If membranes are developed which can take better advantage of the recovered reaction heat, the advantage of reduced input power combined with increased potable water production could create a system with a mass efficiency in the range of 0.8-0.9.

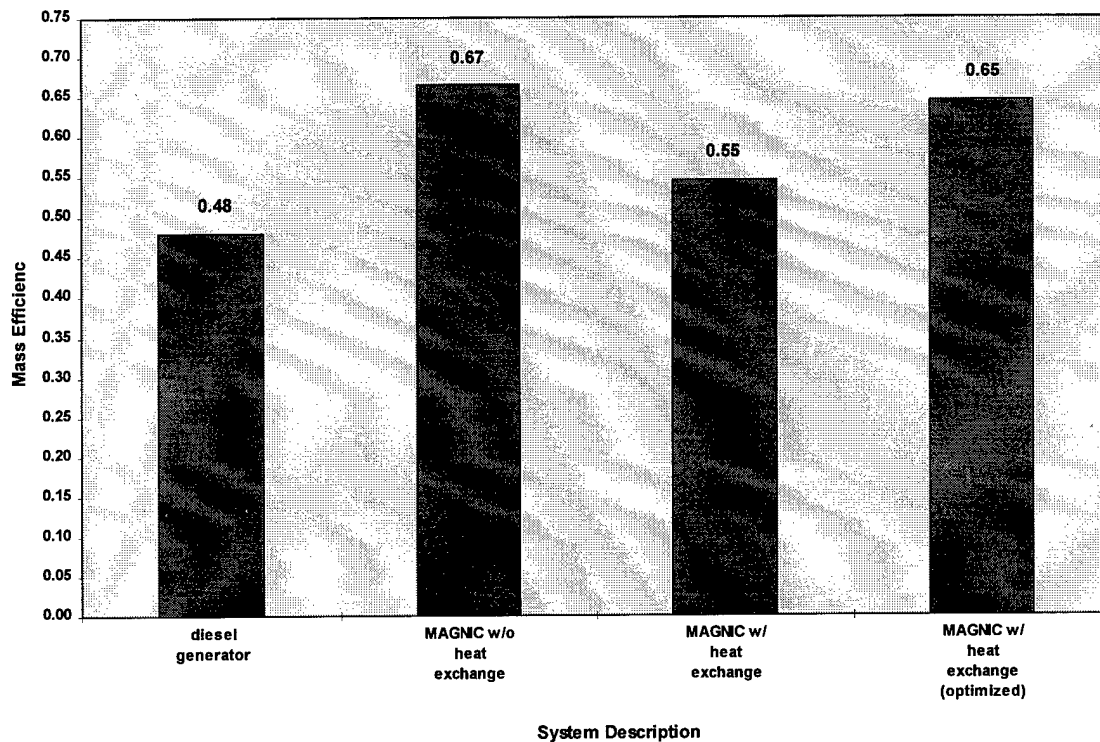


Figure 21: Mass Efficiency Comparison - Diesel and MAGNIC

Table 6. Steady-State System Weights and Mass Efficiencies

Unit	Description	Weight (lbs)	Major Equipment	Water Production (gal/hr)	Mass Efficiency (lbs H ₂ O/lb system)
1	Diesel Desalination Unit	434	Diesel Generator (150 lbs)	25	.48
2	MAGNIC steady-state without heat exchange	313	Reactor (28 lbs) Fuel cell (24 lbs)	25	.67
3	MAGNIC steady-state (non-optimized) with heat exchange ¹	382	Reactor (22 lbs) Fuel cell (24 lbs) Heat exchange (75 lbs)	25	.55
4	MAGNIC steady-state (optimized) with heat exchange ¹	323	Reactor (12 lbs) Fuel cell (24 lbs) Heat exchange (26 lbs)	25	.65

1. Heat exchange consists of recovery from reactor jacket, fuel cell heat exchange, and brine heat exchanger

The use of reduced input power in the steady-state does not address the problem of startup. Initially, the system will require the equivalent hydrogen production of 2.3 kW to start. A suggested solution would be the inclusion of small tank which could accumulate hydrogen over time. The accumulated hydrogen would be used to provide the initial power requirement in a system utilizing heat recovery. First-time startup could be from compressed hydrogen in the same tank. Once the system is warm, recharging the system will maintain the low input power requirement for extended periods of use.

Field Signature

The audible signature for the diesel driven desalination unit presently being used by the Army in field operations is at levels of 85 dB at distances exceeding 12 ft. from the unit. The integrated system emits 69.2 dB at distances of less than 3 ft. from the unit.

No numbers were made available to RTI with respect to the heat signature of the diesel driven desalination unit presently being used by the Army in field operations. However, it is known that combustion temperatures in diesel engines exceed 1300°F with typical exhaust temperatures of approximately 800°F. The fully integrated unit developed by Research Triangle Institute is characteristic of having no temperatures above 220°F.

The desalination system developed by RTI is small in size and may be easily camouflaged to reduce visual signature. The unit was designed in such a fashion that it may be mounted on the back of an M998 (Hum Vee) military vehicle.

Fuel Stability

The fuel for the desalination system developed by RTI is MAGNIC, a magnesium/nickel alloyed metal in solid form. MAGNIC is very similar to aluminum in weight, appearance, and reactivity. MAGNIC forms an oxide layer on its exposed layer, much like aluminum, which makes it resistant to oxidation from atmospheric conditions. It must be in continuous contact with an electrolyte in order to oxidize to the point of deterioration. It may be cast and transported in any shape or size. It may even be used for structural purposes involved in transport such as pallets, crates, etc. It is extremely rugged and does not require careful handling, nor does it require special packaging or containment. It will not leak, spill, produce volatile gases, or contaminate groundwater. It can tolerate any temperature condition including extreme hot and cold temperatures. It will not present added danger to transport personnel, equipment, or otherwise in the event of enemy attack.

Non-Toxic Byproduct

The MAGNIC reaction byproduct, $Mg(OH)_2$, is classified as a weak base with a pH of 10.5. It is used commercially as a waste treatment alkali for acid neutralization. The critical advantage to magnesium hydroxide's use as a waste treatment alkali is the "buffering" capability that

eliminates the risk of increasing the waste stream to a pH of 11 or 12 - a condition detrimental to downstream biological waste treatment systems or aquatic life in surface waters. The maximum pH that magnesium hydroxide can take a waste stream to is 9 which is frequently the upper pH limit for effluent discharges under the Clean Water Act. The magnesium salts resulting from neutralization process with magnesium hydroxide is also non-toxic. In fact, magnesium is a key component of chlorophyll, a compound essential to plant life. It is also a soil nutrient, improving soil porosity under both wet and dry conditions which could be beneficial to land for irrigation. Magnesium hydroxide is not included in any of the hazard categories established by the EPA under Sections 311 and 312 of Title III of the Superfund Amendment and Reauthorization Act of 1986. Due to magnesium hydroxide's classification as a weak base and its non-corrosive nature it is safe and easy to handle with minimum precautions, training, and protective equipment.

2.7 Costs

At present, the cost of the MAGNIC integrated demonstration system, without a fuel cell and weight optimization, is \$10,000.00. A comparable diesel-based desalination unit in use by the Army is \$9000.00. As the previous work has indicated, the MAGNIC system weight can be reduced, with attendant cost reduction. The integrated system was overdesigned for experimental and safety reasons. In particular, use of light materials in a system designed for atmospheric pressure could cut the weight of some portions of the system by 50% or more.

The reverse osmosis unit utilized in the integrated system has fixed commercial cost, in quantities of one, of \$6600.00. Skid costs are related to size, device layout, and instrumentation. Most of the instrumentation used could be eliminated. Compact design of the integrated system is facilitated by the elimination of the bubble condenser, reduced reactor size and weight, and reduction in size and weight of the brine heat exchanger. Estimated cost for a compact skid which fits into a M998 vehicle is \$350.00.

Reactor costs can be reduced in proportion to size. If labor costs are also proportional, a stainless-steel reactor for the non-heat recovery unit could be built for as little as \$950.00. A titanium reactor for the weight-optimized unit with heat recovery could be built for approximately \$800.00. The reduced weight brine heat exchanger, with costs proportional to weight, could be produced for \$300.00. The heavier version of this unit (75 lb) costs \$900.00 when steel construction is used. These numbers are tabulated in Table 7, comparing costs for the diesel unit, the integrated system without heat recovery, and a projection of costs for an optimum-weight integrated system with heat recovery. Fuel cell costs are not included in this projection. Since the size of a fuel cell for any of these units are constant, the fuel cell cost affects the final costs but does not contribute an advantage to any one system.

These estimated costs, combined with the mass efficiency numbers, favor the MAGNIC system without heat recovery over other system combinations. MAGNIC is favored over diesel

generation from either a cost or mass efficiency perspective, regardless of the use of heat recovery.

Table 7: Component and Total Material Costs for MAGNIC and Diesel ROD Systems

Component	Diesel	MAGNIC w/o Heat Recovery	MAGNIC w Heat Recovery, Optimum Weight
Generator	\$1500	NA	NA
Reverse Osmosis Desalination Unit	\$6500	\$6500	\$6500
Reactor	NA	\$950	\$800
Brine Heat Exchanger	NA	NA	\$300
Skid	\$350	\$350	\$350
Total	\$8350	\$7800	\$7950

3. List of Publications and Technical Reports

Magnic Hydrogen Production: Current Status of RTI Feasibility Study and Demonstration, Myers, Patrick, Bob Nelson, and John Cleland, Proceedings of the 8th Annual U.S. Hydrogen Meeting, Alexandria, VA, March 11-13, 1997

References

Myers, P.C., Jr., B. Nelson, and J. Cleland, "MAGNIC Hydrogen Production: Interim Report," Report No. 6357-9602, prepared for Army Research Office by Research Triangle Institute, Research Triangle Park, NC, February, 1996.

Sea Recovery® Reverse Osmosis Desalination System Manual, Sea Recovery Corporation, Gardena, CA, July 1994.